PB-221 335

STEAM STRIPPING ODOROUS SUBSTANCES FROM KRAFT EFFLUENT STREAMS

Bjorn F. Hrutfiord, et al

Washington University

Prepared for:

Environmental Protection Agency

April 1973

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 221 335

EPA-R2-73-196
APRIL 1973

Environmental Protection Technology Series

W73-11060

Steam Stripping Odorous Substances from Kraft Effluent Streams

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

Office of Research and Monitoring

U.S. Environmental Protection Agency

Washington, D.C. 20460

86

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Monitoring, Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

1. Report No. | 2. | 3. Accession No. W73-11060

4. Title: Steam Stripping Odorous Substances From Kraft Effluent Streams (SEKOR),

5. Report Date

6.

7. Author(s): B~~jorn~~ F. Hrutfiord, L~~onnart~~ N. Johanson
J~~oseph~~ L. McCarthy

8. Performing Organization Report No.

9. Organization: University, ~~of~~ Washington
Seattle, ~~Washington~~

10. Project No. EPA Project 12040 EXQ

11. Contract/Grant No.

~~12. Sponsoring Organization~~

13. Type of Report and Period Covered

15. Supplementary Notes: Technology Series
Environmental Protection Agency, report ~~number~~, EPA-R2-73-196, April 1973. 81p, 9 fig, 24 tab, 40 ref

16. Abstract

Laboratory and design studies have been completed relating to volatile constituents which appear in Kraft black liquor and condensate streams, and how these can best be removed and recovered. In order of decreasing concentration, the volatile constituents are alcohols, terpenes, ketones, sulfur bearing compounds, and phenolic compounds. Methanol, the major alcohol contaminant, is found in from 280 to 8400 ppm in condensate streams, amounting to 11 to 16 pounds per ton of pulp produced. Terpenes are found to range from a few ppm to about 4500 ppm in condensates, 4 to 9 pounds per ton of pulp. Acetone is present at concentrations of 2 to 200 ppm, corresponding to 0.07 to 0.4 pounds per ton of pulp. In all, some 40 compounds were ~~found to be~~ present in condensate streams. The feasibility of combining steam stripping of Kraft liquor with steam stripping of condensates was explored, and the conditions under which this may be warranted are reported. Under most present mill situations, steam stripping of black liquor and the last stages of evaporator condensates does not appear to be warranted except in unusual cases. Exploratory type studies were made and are reported concerning improved methods of predicting vapor-liquid equilibria in such systems, and separation of the resulting volatile oils. (EPA)

17a. Descriptors: Steam, ~~Stripping~~, *Pulp, ~~Condensates~~, Pollution Abatement, Water Reuse, ~~Volatiles~~ Recovery, ~~Black Liquor~~, Odor, ~~Control~~. Sulfur compounds, Organic compounds, *Waste water treatment

17b. Identifiers: *Steam stripping, Pulp condensates, *Volatiles, Terpenes, ~~Sulfur Compounds~~, Methyl Mercaptan, Methanol, Turpentine, *Odor control, Black liquor

17c. COWRR Field & Group: 05D

Copy available from GPO Sup Doc as EP 1.23/2, $1.25 ; microfiche from NTIS as PB 221 335 $0.95.

18. Availability

19. Security Class. (Report)

20. Security Class. (Page)

21. No. of Pages

22. Price

Send To: WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U S DEPARTMENT OF THE INTERIOR
WASHINGTON D C 20240

Abstractor: L.N. Johanson | Institution

WRSIC 102 (REV JUNE 1971) GPO 913-244

1a

EPA-R2-73-196
April 1973

STEAM STRIPPING ODOROUS SUBSTANCES FROM KRAFT EFFLUENT STREAMS

By

Bjorn F. Hrutfiord
Lennart N. Johanson
Joseph L. McCarthy

University of Washington
Seattle, Washington 98105

Project 12040 EXQ

Project Officer

Dr. H. Kirk Willard
Pacific Northwest Environmental Research Laboratory
National Environmental Research Center
Corvallis, Oregon 97330

Prepared for

OFFICE OF RESEARCH AND MONITORING
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402
Price $1.25 domestic postpaid or $1 GPO Bookstore

ii

EPA Review Notice

This report has been reviewed by the Water Quality Office, EPA, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

Nature of Steam Volatile Components

The nature of the steam volatile organic compounds which occur in kraft pulp mill aqueous streams has been determined. In order of decreasing concentration, these are alcohols, terpenes, ketones, sulfur bearing compounds and phenolic compounds. Methanol is the main alcohol and was found in concentrations from 280 to 8400 ppm, while ethanol occurred at about 1/10 of these levels. Terpenes were found in ranges from a few ppm to about 4500 ppm. Acetone is the main ketone and occurs from 2 to 210 ppm. Sulfur compounds range from 2 to 800 ppm, based upon prior studies. Combined-stream quantities of these components in lb/ADT are 11.5 to 15.9 for methanol, 0.9 to 2.6 for ethanol, 3.8 to 9.2 for terpenes, 0.07 to 0.4 for acetone.

Process Design Studies

The feasibility of combining steam stripping of black liquor issuing from a continuous Kamyr digester, with steam stripping of condensates was explored. Volatile compound release predictions were made for such a process considering terpenes, terpineols, methanol, and the sulfur compounds, hydrogen sulfide, methyl mercaptan, methyl sulfide and dimethyl disulfide. Black liquor stripping would increase overall stripping costs about two-fold, but would have the advantage of simplifying turpentine recovery and further decreasing odor emanations within the pulp mill and from discharged condensates, as compared with a one to two-column condensate stripping process. An exploratory study has been made of predicting ternary and higher component systems of volatile constituents with water, utilizing binary vapor-liquid and solubility data.

Separation of Oils

The possibility of separation of the turpentine fraction of SEKOR oils from the impurities, chiefly sulfur compounds such as methyl sulfide and

dimethyl disulfide and methanol was investigated. For low concentration of impurities, present methods of oxidative destruction would appear preferable. For higher concentrations fractional distillation may be promising if only α-pinene is to be recovered. Solvent extraction does not appear to be promising: selective adsorption, using silica gel in preference to molecular sieves, may be feasible for higher concentrations of impurities.

This report was submitted in fulfillment of project 12040EXQ under the sponsorship of the Environmental Protection Agency in cooperation with the University of Washington, Seattle.

CONTENTS

Section		Page
I	Conclusions	1
II	Recommendations	3
III	Introduction	5
IV	Objectives and Plans	7
V	Nature and Concentration of Steam Volatile Compounds	9
VI	Process Design Studies	31
VII	Separation of SEKOR Oils	65
VIII	Acknowledgements	73
IX	References	75
X	Publications and Patents	79
XI	Glossary	81

FIGURES

		Page
1	FORMATION OF METHANOL, ETHANOL AND ACETONE IN LABORATORY KRAFT COOKS OF DOUGLAS FIR	18
2	SCHEMATIC OF SAMPLE SITES FOR BATCH AND CONTINUOUS PROCESSES	20
3	FLOW SYSTEM FOR COMBINED STEAM STRIPPING STUDY UTILIZING HEAT FROM BLACK LIQUOR STRIPPING	34
4	FLASH CONCENTRATION AND OXIDATION STEPS IN BLACK LIQUOR RECOVERY	40
5	MULTIEFFECT EVAPORATION STAGES AND DIRECT CONTACT EVAPORATION	42
6	TERNARY LIQUID EQUILIBRIUM RESULTS AT 25°C. WATER PINENE METHANOL	60
7	TERNARY LIQUID EQUILIBRIUM RESULTS AT 100°C. WATER PINENE METHANOL	60
8	TERNARY LIQUID EQUILIBRIUM RESULTS AT 100°C. WATER DIMETHYL SULFIDE METHANOL	61
9	TERNARY LIQUID EQUILIBRIUM RESULTS AT 100°C. WATER-TERPINEOL-METHANOL	61

TABLES

No.		Page
I	Organic Compounds in Kraft Mill Condensate Streams	10
II	Estimated Composition of Kraft Mill Streams	13
III	Methanol Content of Some Condensate Streams from a Pacific Northwest Kraft Mill	14
IV	Total Yields of Methanol, Ethanol and Acetone from Laboratory Kraft Cooks	16
V	Concentration and Total Turpentine in Kraft Mill Condensate Streams	22
VI	Flow of Condensate Streams in the Kraft Pulp Mill Process	23
VII	Material and Energy Balance for Kamyr Digester, Washers, and Flash System	35
VIII	Tower Height and Process Steam Requirements for Methyl Mercaptan Removal by Steam Stripping of Black Liquor	38
IX	Removal of Volatile Constituents by Steam Stripping of Kraft Black Liquor	38
X	Operating Parameters of Black Liquor Stripping Column for Cases Extended to Steam Stripping of Condensates	41
XI	Summary of Volatile Component Distribution - Case I	44
XII	Summary of Volatile Component Distribution - Case IIa	45

TABLES (CONT'D)

No.		Page
XIII	Summary of Volatile Component Distribution - Case IIb	46
XIV	Summary of Volatile Component Distribution - Case III	47
XV	Case IIa - Composition of Feed and Product Streams of SEKOR A Columns	48
XVI	Case IIa - SEKOR A Column Design For Condensate Stripping	49
XVII	Case IIa - Composition of Feed and Product Streams, SEKOR Column C Stripping Evaporator Condensate	49
XVIII	Case IIa - SEKOR Column C Design For Evaporator Condensate Stripping	50
XIX	Comparison of Contaminant Content of Condensate Without and With Steam Stripping	50
XX	Water-Organic Binary System Results	57
XXI	Methanol-Organic Binary System Results	58
XXII	Summary of Margules Equation Constants For Binary Systems	59
XXIII	Summary of Renon Equation Constants For Binary Systems	59
XXIV	Summary of Break-through Data for Selective Adsorption of Dimethyl Disulfide from Terpenes	71

SECTION I

CONCLUSIONS

Characteristics of Steam Volatile Compounds

1. Methanol, ethanol, acetone and traces of other water soluble organic compounds are quantitatively the most important steam strippable organic compounds in condensate streams.
2. Turpentine, characterized by α-pinene and especially α-terpineol is the second most important group of steam volatile organic compounds found in condensate streams.
3. Sulfur bearing compounds do not occur in large concentrations, but are important owing to their odor characteristics.
4. Effective stripping of turpentine decanter underflow and of blow condensate would control about three-fourths of the total steam volatile compounds in kraft mill streams.

Design Studies

1. Steam stripping of black liquor under moderate pressure (under 100 psia) appears feasible on the basis of preliminary design study.
2. Terpenes, methyl mercaptan, and methyl sulfide can be largely stripped out of black liquor in such a column.
3. Overhead vapors generated are sufficient to serve as a heat medium for steam stripping of condensates through the first two multi-effect evaporator stages.
4. Methanol is stripped out of black liquor and condensates with difficulty, appearing in the evaporation train through the first two multi-effect stages, and in the air effluent from weak liquor oxidation.
5. Incorporation of black liquor stripping in a kraft system utilizing condensate steam stripping would increase overall costs approximately two to three-fold, relative to costs of steam stripping only condensates.

Oil Separations

1. The separation of the turpentine fraction of SEKOR oils from the sulfur compounds by solvent extraction does not appear promising.
2. The separation of the turpentine fraction from sulfur compounds utilizing selective adsorption was found to be technically feasible on a laboratory scale.
3. Silica gel will selectively retain sulfur compounds allowing their removal from terpenes in a packed column system.
4. Synthetic zeolites of 10 to 13 angstrom pore size also selectively adsorb sulfur compounds relative to terpenes, but less effectively than silica gel.

SECTION II

RECOMMENDATIONS

All decanter underflow streams as well as blow gas condensate from batch kraft pulping processes and analogous streams from continuous processes should be steam-stripped for removal and control of volatile organic compounds.

Decisions on steam stripping of other condensate streams should be made on an individual mill basis. For example, if methanol is to be reduced to levels below the equivalent of 2.0 lb methanol/ADT of pulp, then two columns should be used, stripping the first two evaporator stage condensates in addition to the higher concentration condensates.

Steam stripping will be superior to air stripping of condensates for the majority of installations and should be used in all except the unusual cases, in which the effluent air can be utilized in furance combustion.

Steam stripping of black liquor would appear to be advantageous only for extreme situations of removal and recovery of volatile constituents.

SECTION III

INTRODUCTION

Study of the steam stripping of Kraft Pulp Mill effluent streams began over a decade ago in the laboratories of the Chemical Engineering Department of the University of Washington. These investigations were conducted largely through the "Pulp Mills Research Program" of this University, financed in part by the Northwest Pulp and Paper Association. Results were reported to this sponsoring organization and in part have since been published as three papers under the acronym SEKOR (Stripping Effluents for Kraft Odor Reduction) as SEKOR I, II, and III (TAPPI Magazine, 50 No. 2, pp 82-85, February 1967; 50 No. 2, pp 86-91, February 1967; and 50 No. 6 pp 270-275, June 1967). Part of the study (reported in SEKOR II) was a cooperative venture with the St. Regis Company at their Tacoma, Washington Kraft Mill, in which the steam stripping of condensates was successfully demonstrated in a bench-scale continuous pilot plant.

Fellicetta, Peniston and McCarthy first identified the major odorous constituents in such condensate streams (TAPPI 36 425, 1953) as hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. This finding has since been verified in mills and laboratories throughout the world. The SEKOR process provides a means of concentrating these and other non-aqueous constituents, to allow disposal or further processing and thus remove them from effluent waters.

While initial emphasis in the steam stripping study was aimed at removal and control of odorous compounds, it has been apparent for some time that significant amounts of other steam volatile compounds are present in kraft pulp mill aqueous streams. The SEKOR I paper pointed out the presence of significant amounts of turpentine in the originally

Preceding page blank

isolated oils, and analysis of aqueous condensate revealed the presence of various alcohols and ketones of low molecular weight. These classes of compounds are not of importance from the viewpoint of odor, but are very important in mill effluent due to the major BOD load caused by the methanol etc., and the turpentine is not particularly desirable in that certain compounds in this class may be toxic to marine organisms.

With this general background, enough was known to define what further information was needed for design of removal equipment. Concerning the compounds to be encountered, additional information on their nature and properties was required as well as information on concentration ranges in the several streams to allow decisions as to which streams should be processed and what compounds to expect in the stripped material. Sizing of equipment could proceed from this information, as well as the somewhat more difficult problem of defining operating procedures.

Earlier reported work demonstrated the feasibility of stripping condensates, and the present study extended these studies and included as well an analysis of application of steam stripping to black liquor, since this is the stream in which all volatile compounds are present.

Fractionation of the resulting stripped-out oils presented a special problem, and basic investigations into separation methods were also a part of this study.

SECTION IV

OBJECTIVES AND PLANS

For the past three years, this work has been continuing at the University of Washington under the sponsorship of the Research and Monitoring Office of the EPA. The goal of this program was to develop sufficient fundamental data and design information to allow the design of SEKOR process modifications for a variety of industrial situations. Inherent in the study was the improvement of process economics and means of recovery of values such as hot reusable water and chemicals, in order that the process may be made as attractive as possible for adoption within the Kraft pulping industry.

The three specific aims of the research program were:

(a) To secure further information concerning the nature and concentration of steam-volatile substances present in Kraft pulp mill black liquors and condensates arising from a number of species of wood and under several process conditions;

(b) To conduct further laboratory experiments and SEKOR process design studies in order to evaluate several alternative ways of conducting the SEKOR process and to permit the optimum procedure or procedures to be identified; and

(c) To conduct laboratory and process design studies directed toward the development and evaluation of procedures by which SEKOR oils, arising under various conditions, can be separated on an industrial scale into components or fractions which may be sold to return a significant income to offset the costs of conducting the SEKOR process.

A further part of the objectives and plans for the study comprised collaboration with representatives of the Weyerhaeuser Company. A joint plan of work was developed and made known to representatives of

Environmental Protection Agency. Many discussions and conversations occurred and yet at the time of conclusion of the present study, it had not yet been possible for representatives of the Weyerhaeuser Company to proceed with development of the contemplated pilot plant and thus, this phase of our original plan could not be carried out. Meanwhile, complementary attention was devoted to other phases of the activity, and this is set forth below.

SECTION V

NATURE AND CONCENTRATION OF STEAM VOLATILE COMPOUNDS IN KRAFT PULP MILL PROCESS STREAMS

Introduction

The general plan for this part of the study was to survey kraft pulp mill aqueous streams for steam volatile organic compounds and to identify as many of them as possible. Following identification, the concentration range in which the more important of these organics occurred was determined, especially in the several condensate streams in the mill.

Samples were obtained from a wide variety of sources, from a number of Northwest pulp mills. Basically these covered the main variables of individual streams in batch and continuous processes and also the influence of wood species being pulped. Effort was concentrated on condensate streams such as digester relief condensate, blow gas condensate and evaporator condensate in batch processes, and their equivalent flash tank vapors and evaporator condensates in continuous processes. Some other more concentrated samples were also studied, i.e. crude sulfate turpentine and black liquor from various mills.

Identification of Steam Volatile Compounds

A summary of the organic compounds identified in our studies is presented in Table I. Many of the compounds listed have also been identified by others.

TABLE I

Organic Compounds in Kraft Mill Condensate Streams

Alcohols
- Methanol
- Ethanol
- 1-propanol
- 2-propanol
- Butanol
- 2-methyl-1-propanol

Ketones
- Acetone
- 2-butanone
- 3-pentanone
- 3-methyl-2-butanone
- 4-methyl-2-pentanone
- 2-heptanone

Phenols
- Guaiacol
- Phenol
- Syringol
- o-Cresol
- m-Cresol
- p-Cresol
- Acetovanillone

Sulfur Bearing
- Methyl Mercaptan
- Dimethyl Sulfide
- Dimethyl disulfide
- Thiophene

Terpenes and Related Compounds
- α-pinene
- Camphene
- β-pinene
- Mycrene
- Δ^3-carene
- α-phellandrene
- α-terpinene
- Limonene
- β-phellandrene
- ∂-terpinene
- Terpinolene
- Fenchone
- Linalool
- Fenchyl alcohol
- Terpinene-4-ol
- α-terpineol
- 2-methylfuran
- Toluene
- 4(p-tolyl)-1-pentanol

The sulfur containing compounds were well known and were verified as present in oils isolated from condensates by steam stripping in our earlier studies (1). The presence of the major alcohols, methanol and ethanol, were also verified in the earlier work and additional identification of trace components has been made by Bethge and Ehrenborg (2). The major ketone acetone has long been known to be present in condensates, and the next most important ketone quantitatively, 4-methyl-2-pentanone, had been identified earlier by infra-red methods (1). Ketones found in trace quantities and some additional trace compounds are reported in the present study. Of the phenolic compounds, guiacol is the main compound found and was reported earlier (4). The remaining phenolics have been verified in our studies here and by others (4, 5). The terpenes in condensate streams were identified in our prior studies (1) and have been verified in detail in more recent work (6). Numerous other organic compounds are present in trace amounts.

These compounds have been isolated by steam distillation followed by separation from water by solvent extraction or fractionation and sometimes by selective chemical reactions. In earlier work infra-red spectroscopy was used for identification and this has been replaced by use of gas chromatography-mass spectrometry in more recent studies. Details are presented in the references listed (2, 3, 6).

The formation of these compounds will be discussed later. At this point it is useful to recognize that most of these classes of compounds, i.e., sulfur bearing compounds, alcohols, ketones, and phenols are the result of wood treatment and especially of reactions occurring during the pulping process and will be found in all kraft mills. Only the terpenes are characteristic of the wood species being pulped. Thus the main qualitative differences will occur in this class of compounds. Quantitative differences are more a function of process operation and equipment design and will also occur.

Concentration Ranges of Steam Volatile Compounds

Concentration ranges for sulfur bearing compounds in condensate streams have been well documented in the literature and were not studied (7). These ranges are methyl mercaptan (2-250 ppm), dimethyl sulfide (10-800) and dimethyl disulfide (2-140).

The concentration of methanol, ethanol and acetone in condensate streams from the pulping of pine and birch has been reported from various mills and these values taken from the literature are summarized in Table II. In order to estimate the total methanol, etc., produced, the flow rates of the individual condensate streams must be known. These were unavailable and therefore a calculation was made based on the estimated quantities of 232, 2030 and 12,775 lbs of water per air dried ton (ADT) of pulp for the digester relief, blow, and evaporator condensates respectively. These represent typical values from U.S. kraft mills (11). The total methanol yields resulting from the concentrations reported in Table II are then about 11 to 16 lbs methanol/ADT from pine and about 11 lbs methanol/ADT from birch. Estimates of total ethanol and acetone are also presented in Table II.

Methanol Content of Kraft Mill Condensate Streams

Methanol concentration was determined for condensate samples from a mill pulping several wood mixes in order to provide further information on the effect of wood species and on the total amount of methanol formed (12). This study was limited to methanol since its quantity is an order of magnitude greater than the next most abundant compound (ethanol) and since it makes the greatest single contribution to BOD (9). The concentration of methanol, based on the same material balance used for calculating the data in Table II, are summarized in Table III. The data show that the methanol content of digester relief

TABLE II

Estimated Composition of Kraft Mill Streams

Condensate Stream	Wood Species Pulped: Pine (8,9,10)	Birch (8)
Digester Relief		
Methanol ppm	5900-7500	7100
(lb/ADT)*	(1.4-1.7)	(1.6)
Ethanol ppm	700-1500	1600
(lb/ADT)*	(0.2-0.4)	(0.4)
Acetone ppm	60-210	120
(lb/ADT)*	(0.02-0.05)	(0.03)
Blow Gas		
Methanol ppm	390-960	525
(lb/ADT)*	(0.8-1.9)	(1.1)
Ethanol ppm	60-670	25
(lb/ADT)*	(0.1-1.4)	(0.05)
Acetone ppm	10-60	5
(lb/ADT)*	(0.02-0.1)	(0.01)
Evaporators		
Methanol ppm	725-960	625
(lb/ADT)*	(9.3-12.3)	(8.0)
Ethanol ppm	50-60	15
(lb/ADT)*	(0.6-0.8)	(0.2)
Acetone ppm	2-12	5
(lb/ADT)*	(0.03-0.2)	(0.06)
Total Condensates		
Methanol lb/ADT	11.5-15.9	10.7
Ethanol lb/ADT	0.9-2.6	0.7
Acetone lb/ADT	0.07-0.4	0.10

*Conversion from parts per million to pounds per air dried ton of pulp is based upon a nominal material balance giving 232 lb/ADT relief condensate, 2030 lb/ADT blow condensate, and 12,775 lb/ADT evaporator condensate (11).

TABLE III

Methanol Content of Some Condensate Streams from a Pacific Northwest Kraft Mill

Condensate Stream	Alder-Douglas fir (≈4:1)	Cedar-Douglas fir (≈4:1)	Douglas fir (100%)
Digester Relief Condensate			
methanol ppm	8400 ± 400 [2]*	2900 ± 100 [2]	2800 ± 400 [2]
lb MeOH/ADT	2.0**	0.7	0.7
Blow Gas Condensate			
methanol ppm	2000 ± 600 [3]	1800 ± 100 [3]	2100 ± 300 [2]
lb MeOH/ADT	4.1	3.7	4.3
Evaporator Condensate			
methanol ppm	410 ± 20 [2]	410 ± 20 [2]	280 ± 20 [2]
lb MeOH/ADT	5.2	5.2	3.6
Total Methanol			
lb/ADT	11.3	9.6	8.6

*Methanol concentrations are reported in ppm (or mg/liter) together with the approximate spread of data and the number of samples upon which the result is based.

**Flow quantities were not available from the pulp mill. The ppm values were converted to a total weight basis (lbs/ton of air dried pulp) by using a typical balance of 232, 2,030 and 12,775 lbs of water/ADT of pulp for digester relief condensate, blow gas condensate, and evaporator condensate respectively (11).

from alder cooks is similar to values from birch cited in Table II, while prior values for pine are greater by a factor of two than values reported here for Western red cedar and Douglas fir.

Blow gas condensate concentrations and amounts in Table III are uniformly higher than previously reported values of Table II, while evaporator condensate values are lower. This probably reflects a difference in the process conditions relative to blow condensate. Differences in extent of water recycle and direct contact evaporators, for instance, are not taken into account in Tables II and III, and these would obviously effect concentration. The total methanol content of all condensates are of comparable magnitude in Table II and III, of about 8 to 12 lb/ADT.

The alcohols are quantitatively very important among the organic compounds in mill condensates. Methanol is the main alcohol found and is also the main organic compound, often reported in concentrations as high as 0.5% in digester relief condensates. It is extremely important in overall mill effluent BOD.

Effect of Wood Species on Methanol Formation

The effect of pulpwood species on the amount of methanol formed in kraft pulping was studied in more detail by carrying out laboratory cooks. Mill samples are unsuitable for this purpose for several reasons, among which are the unavailability of condensates from pulping of a single wood species, different cooking cycles with different pulpwood mixes and difficulties in determining adequate material balances on condensates. The results from the laboratory cooks on the four woods are summarized in Table IV which also includes results for ethanol and acetone. There are significant differences in the total amount of methanol formed, ranging from about 28 lbs/ADT from the hardwood Red alder to about 14 lbs/ADT for Douglas fir. The trend in the quantity of methanol formed is similar to the total

methoxyl content of the wood, which is reasonable since most of the methanol is formed with 4-O-methyl glucuronic acid residues, typically greater in hardwoods.

TABLE IV

Total Yields of Methanol, Ethanol and Acetone from Laboratory Kraft Cooks

Wood Species	Methoxyl Content, %	Methanol	Ethanol	Acetone
Red Alder	(+)	27.8*	1.7*	0.3*
Western red cedar	5.58	26.2	1.4	0.4
Western hemlock	5.0	15.6	1.7	0.3
Douglas fir	4.42	14.4	2.3	0.4

* All values are in lbs/ADT of pulp

\+ Not available but considered higher than softwood methoxyl content

Ethanol does not show a trend which can be related to wood species, which is expected since it is formed primarily by fermentation in the wood after felling, and is thus dependent on chip pretreatment (13). Generally, the ethanol forms rapidly under anaerobic conditions, reaching a maximum in a week or so. The reaction is slower under aerobic conditions. Ethanol is lost fairly rapidly on storage. Acetone, the origin of which is not well defined, also shows no trend with wood species. The ethanol and acetone by-products are present in much smaller quantities than methanol.

Comparison of Methanol, Ethanol and Acetone Yields with Commercial Results

The trends in the total amount of methanol formed from different wood species in mill pulping agrees with that found in laboratory cooks. The order of magnitude of the differences is, however, not as great as

expected based upon the laboratory cooks. This may be explained in part by the fact that the mill samples result from pulping of mixtures. The estimated wood ratio used for the particular samples, shown in Table III, will tend to decrease the magnitude of the species differences. A more important factor is likely to be the difference in pulping conditions used for softwoods versus hardwoods.

The reaction forming methanol is

$$R\text{-}OCH_3 + NaOH \rightarrow R\text{-}ONa + CH_3OH \qquad \text{Eq.1}$$

and probably is a second order S_N2 type of reaction. The rate expression for forming methanol would then be

$$\text{Rate} = k\,[R\text{-}OCH_3]\,[OH^-] \qquad \text{Eq.2}$$

The rate constant has not been determined. However a brief study of the rate of formation of methanol, ethanol and acetone was made by pulping Douglas fir and determining the cumulative content of these compounds at several time intervals during the cooking cycle. The results are shown in Figure 1. The curve for methanol formation from wood is similar to the results from hemicellulose reported by Clayton (14). Methanol formation is still occurring at the end of a normal cooking time and shorter cooking cycles will result in less methanol being formed. Lower temperatures and lower pulping pH also have the same effect. In commercial pulping of hardwoods all of these cooking parameters are reduced, resulting in less methanol being formed despite the higher potential with hardwoods. The ethanol concentration remains constant after about one hour of reaction time in agreement with a fermentation route of formation prior to the cook as the main source of this compound. Acetone, present in low concentration, is actually declining in concentration after the first hour of reaction time, indicating loss, in all probability, by a condensation reaction.

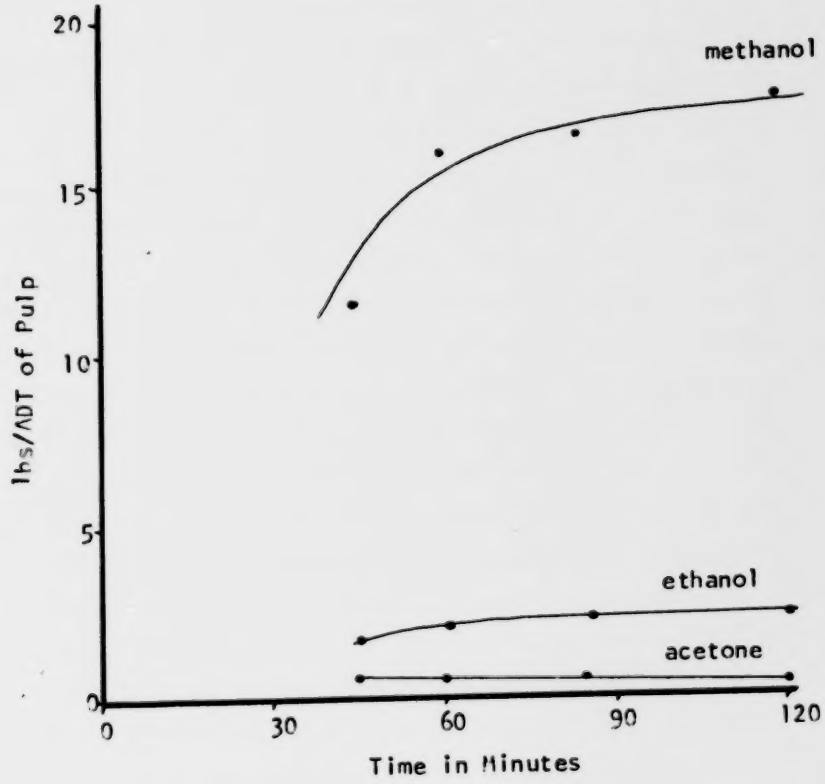


FIGURE 1. Formation of Methanol, Ethanol and Acetone in Laboratory Kraft Cooks.

17°C, 20% active alkali, 25% sulfidity, 6/1 liquor/wood

The difference in absolute magnitude between the methanol quantities found in laboratory cooks and in mill streams may be due to several factors, the most important of which is the significant difference in pulping conditions. More complete recovery of volatiles possible from the laboratory black liquor and departures of industrial processing from the assumed material balance may also be important. The large differences involved do suggest estimates of the methanol content of kraft process streams are perhaps generally conservative.

Turpentine Concentration

Condensate water is often contaminated with turpentine. Usually crude sulfate turpentine is collected from digester relief gas by condensation and turpentine separation in a decanter. The decanter underflow contains the greatest concentration of turpentine of any stream in the process. There are many other turpentine containing streams in a mill and large variations in concentration can occur in these streams, dependent on design and especially on operation variables.

A survey of turpentine concentrations was undertaken in which a variety of water samples were collected from four mills in the Pacific Northwest and British Columbia. Usually a number of samples were collected from the same source over a month's operating time so that what might be called normal operating ranges could be established. Actual sampling sites are shown in Figure 2, which is a composite schematic of the essential features of the mills sampled. Both batch and continuous systems were included in the study with the continuous operation systems including latest technology high turpentine yielding systems (16, 17).

Sample sites 1, 2 and 3 in Figure 2 are for batch processes and represent digestor relief, blow and evaporator condensate; sample were actually taken from the turpentine decanter underflow, the heat recovery accumulator, and evaporator condensate respectively.

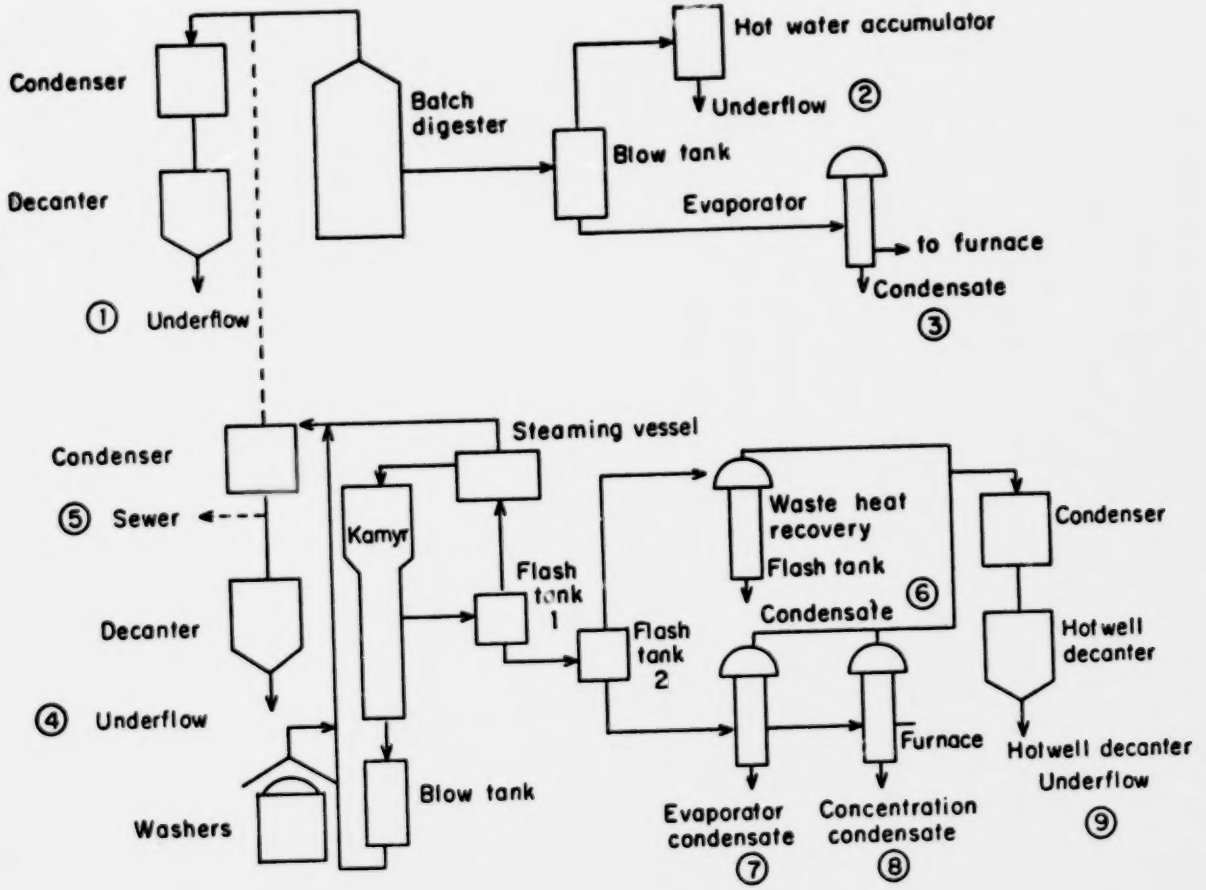


Figure 2. Sample sites for batch and continuous processes

Sample sites 4 and 5 include condensate originating from the #1 flash tank of a Kamyr system via the steaming vessel. Sample #4 is from a turpentine decanter underflow and #5 is condensate from a system where heat recovery is practiced but no turpentine is recovered.

Samples 6, 7, 8 and 9 originated from the further processing of black liquor. Samples 6 and 7 were from early stages in the evaporators; 8 was from the final stages of evaporation and 9 was a decanter underflow sample. Many interconnections exist in the system and changes in operating variables may be expected to greatly influence the concentration of turpentine in the several streams.

The results of this survey are summarized in Table V which lists concentrations of turpentine found in the various streams and also the total turpentine represented by this stream in lbs/ADT of pulp produced. The latter figure is calculated from the concentration and from the flow rate of the stream. We were able to obtain estimates from mill personnel of flow rates for each of the streams sampled and these along with the NCASI survey averages (11) are listed in Table VI. Further details of survey techniques used may be found in reference (15).

Batch Systems

The turpentine concentration has been determined in a number of individual samples of decanter underflow water obtained from four different mills. Each mill was fairly consistent, but very large differences were found between mills. The highest concentration observed was about 5400 ppm and all samples from this mill averaged 4500 ppm. A second mill averaged about 1500 ppm and two other mills averaged about 435 ppm. These mills all pulp similar wood mixes including Western Hemlock, Douglas Fir, and some Ponderosa pine plus some other species. Most pine is pulped at Mill A, (≈25%) which has the highest underflow concentration. The ten-fold difference found between these mills cannot be explained based only on species differences and must

TABLE V

Concentration and Total Turpentine in Kraft Mill Condensate Streams

Sample No.*	Process Stream	Mill Designation A	B	C	D
1	Batch Decanter Underflow Turpentine, ppm (lb/ADT)	4514 ± 950 (4)** (2.02)	1490 ± 300 (4) (.37)	430 ± 90 (4)	444 ± 5 (2)
2	Hot Water Accumulator Turpentine, ppm (lb/ADT)	665 (1) (2.98)	208 (1) (.63)	---	---
3	Evaporator Condensate Turpentine, ppm (lb/ADT)	106 (1) (.50)	23 (.31)	---	---
4	Steaming Vessel Decanter Underflow Turpentine, ppm (lb/ADT)	580 ± 155 (3) (.23)	---	---	---
5	Sewered Steaming Vessel Condensate Turpentine, ppm (lb/ADT)	---	1493 (1) (1.39)	---	---
6	#2 Flash Tank Condensate Turpentine, ppm (lb/ADT)	105 (1) (.33)	---	---	---
7	Evaporation Condensate (Kamyr) Turpentine, ppm (lb/ADT)	146 (1) (2.49)	---	---	---
8	Concentration Condensate Turpentine, ppm (lb/ADT)	307 (1) (.61)	---	---	---
9	Hotwell Decanter Underflow Turpentine, ppm (lb/ADT)	616 ± 350 (3) (.04)	---	---	---

*Sample sites shown in Figure 2
**Spread of data and number of samples analyzed

TABLE VI

Flow of Condensate Streams in the Kraft Pulp Mill Process, (Results in lb/ADT)*

Sample No.		Mill Designation A	B	C	D	NCASI
1	Batch Decanter Underflow	448	253	230	230	232
2	Hot Water Accumulator	4,482	3,023	---	---	2,030
3	Evaporator Condensate	14,061	13,300	---	---	12,775
4	Steaming Vessel Decanter Underflow	398	----	---	---	----
5	Sewered Steaming Vessel Condensate	----	930	---	---	----
6	#2 Flash Tank Condensate	3,186	----	---	---	----
7	Evaporator Condensate (Kamyr)	17,074	----	---	---	----
8	Concentrator Condensate	1,991	----	---	---	----
9	Hotwell Decanter Underflow	64	----	---	---	----

*Flow data are based on average values from the mills involved

be due to differences in equipment and operating practice. We were able to obtain straight line correlations between sodium concentration and turpentine concentration on batch decanter underflow, supporting the idea of turpentine being emulsified by black liquor carryover. Losses of turpentine via the underflow can be significant; e.g. mill A may lose up to 2 lbs/ADT in this stream.

As expected, the concentrations of turpentine found in blow condensate are lower than those found in decanter underflow. Values of 665 and 208 ppm were found in two mills in the accumulater water. The amount of turpentine found here will vary due to differences in digester steaming practices and equipment design. For example, one mill studied uses a vaporshere for control of noncondensables from the blow, and condensate from this system is returned to the digester relief turpentine decanter instead of to the hot water accumulater. On the other hand, another mill was operating at reduced production rates and was doing less relief gas venting, thus increasing the amount of turpentine in the accumulator water. Samples of evaporator condensate generally contain very little turpentine; 106 and 23 ppm were found in two samples.

The total turpentine found in mills A and B in these three condensate streams has been calculated, Table V, and is 5.5 lbs/ADT in mill A and 1.31 lbs/ADT in mill B. It is important to recognize that these values depend on accurate flow measurement which is difficult in an operating mill. Referring to Table VI, the flow values reported for the various streams in mill A are generally much higher than the average values found in surveys done by the NCASI (11). Mill A and also mill B tend to have high rates of condensate flow, and this may be characteristic of Western mills as opposed to Southeastern mills. It is apparent that the blow condensate is the more important stream in total turpentine quantity despite the lower concentration. If both decanter underflow and blow condensate were effectively steam stripped,

75 to 90% of the turpentine lost could be recovered. Recovery of this turpentine by air stripping is not easible.

Continuous Processes

Decanter underflow, originating from the #1 flash tank and steaming vessel condensate, was found in one mill to contain 580 ppm turpentine. In a second mill, heat is recovered from this stream but a turpentine decanter is not used and the condensate was found to contain 1493 ppm turpentine. In terms of total turpentine, the decanter underflow represents a negligible 0.23 lbs/ADT, while the unseparated condensate represents 1.39 lbs/ADT of turpentine.

In the continuous process, only a part of the available turpentine is removed from the black liquor via the steaming vessel and recovery of the remainder requires processing of a number of streams including washer vents (17). Whatever turpentine is available from these vents and from the blow tank is returned to the steaming vessel decanter in the mill studied. Remaining turpentine in the black liquor is routed to a separate decanter, condensate here originates from the #2 flash tank, several points in the evaporators and other sources. This decanter underflow contained 616 ppm turpentine, and this value combined with the low flow rate shows very low loss of turpentine via this route.

Samples of condensates from the first evaporator stages were analyzed and these show relatively low turpentine concentrations in the 100 to 150 ppm range. The flow rates are high here, especially on Sample 7 and an appreciable amount of turpentine is lost in this condensate. Concentrator condensate, Sample 8, analyzed 307 ppm, and another high flow rate is reported for this stream. Altogether, the evaporator condensates contain about 2.4 lb/ADT of turpentine, and thus are about as important in turpentine losses as batch blow condensate and decanter underflow. Comparisons of this kind are not as meaningful as would be

desired because of the extensive recycle and reuse of condensate water, which are factors not considered in detail in this study.

Origin of Steam Volatile Organic Compounds in Kraft Mill Streams

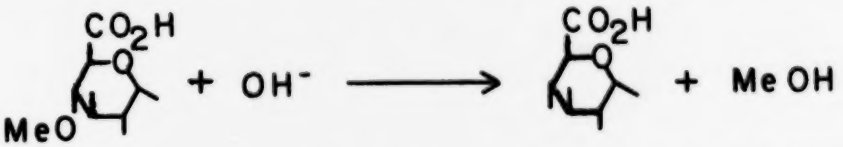
Understanding of the origin of the organic compounds of interest may lead to ways of controlling their formation and release. Of the main classes identified (Table I) methyl mercaptan and its derivatives are the most objectionable. The chemistry of their formation and physical phenomena related to their release has been extensively studied and is reviewed elsewhere (7). Briefly, methyl mercaptan is formed by a reaction between lignin methoxyl groups and hydrosulfide ion (Eq. 3), dimethyl sulfide is formed by a similar reaction (Eq. 4) and the disulfide is an oxidation product (Eq. 5).

$$\text{Lig-O-Me} + SH^- \longrightarrow \text{Lig } O^- + \text{MeSH} \qquad \text{Eq. 3}$$

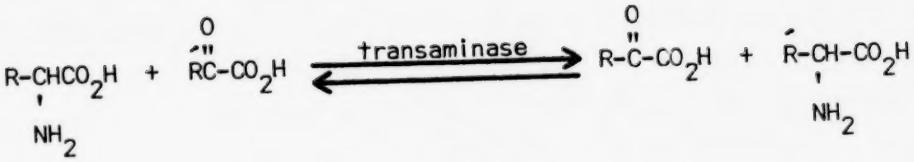
$$\text{Lig-O-Me} + MeS^- \longrightarrow \text{Lig } O^- + \text{MeSME} \qquad \text{Eq. 4}$$

$$2MeS^- + [O_2] \longrightarrow \text{MeSSMe} \qquad \text{Eq. 5}$$

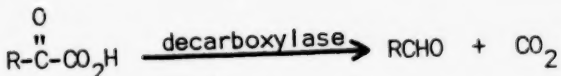
Methanol is believed to arise via alkaline hydrolysis of 4-O-methyl glucuronic acid residues in hemicellulose (Eq. 6), as discussed earlier.



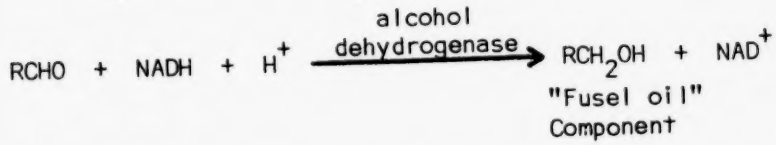
It has now been established that ethanol is present in wood chips prior to pulping (13). Apparently anaerobic conditions develop in the log as water transport is disrupted and some ethanol is formed via glycolysis as this condition develops. Usually the ethanol can be detected a week or two after felling of the tree (18). Some ethanol will be lost by volatilization from the chip and the remainder will then be steam distilled off during pulping. Several higher alcohols have been found in trace amounts (2), these alcohols are for the most part normal components of fusel oil. This kind of alcohol is derived from amino acids, or their precursors, by a process of deamination, decarboxylation and reduction, Eq. 7 a, b, c.



Eq. 7a

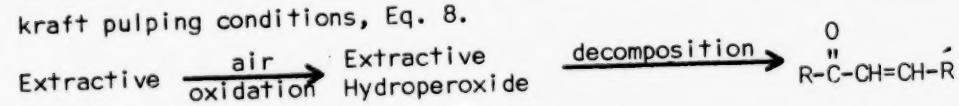


Eq. 7b

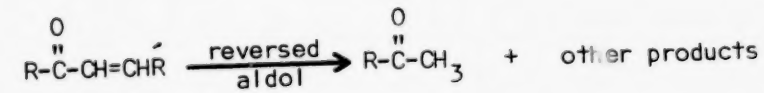


Eq. 7c

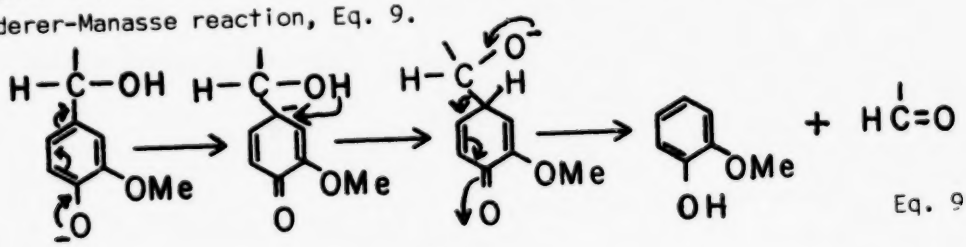
All of the ketones reported from kraft mill streams are methyl ketones, CH_3CO-R, which are formed by air oxidation of extractives, followed by decomposition of the extractive hydroperoxide to an α, β-unsaturated ketone, which in turn may undergo a reversed aldol reaction under the kraft pulping conditions, Eq. 8.



Eq. 8



For the phenolic compounds, guaiacol is the main compound reported in condensate streams. Others indicated as present are phenol, syringol, cresols, vanillin and acetonvanillone. Guaiacol and syringol are more readily volatile with steam and usually are found in evaporator condensates. They are probably formed from structural elements in lignin having free phenolic and α-hydroxyl groups via a reversed Lederer-Manasse reaction, Eq. 9.



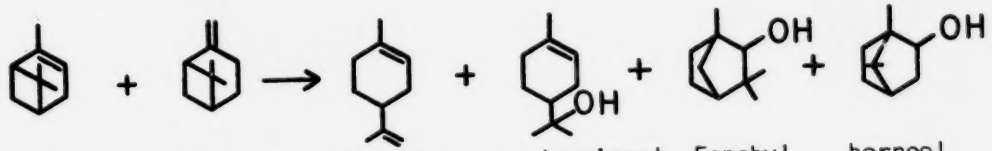
Eq. 9

Guaiacol and related phenolics such as the cresols have not received the attention they deserve in control of odor as well as toxicity. Most people recognize that the overall odor of a kraft mill is "different" from that of the well known sulfur bearing compounds, and one can usually distinguish a "burned or typical" odor near the mill. This is probably due to phenols in the evaporator condensate (5). Guaiacol is the main phenolic component present in this stream, and using the data of Marvell and Wiman (4) a concentration of about 10 ppm may be estimated for evaporator condensate from the pulping of Douglas fir. Since the odor threshold for guaiacol dissolved in water is reported to be 0.021 ppm (19), guaiacol should be readily detectable. Paracresol, probably present in much lower concentration, since it is barely detectable, has an odor threshold value of 0.001 ppm in air and probably is also important (20). These compounds are described as having burned, smoky, phenolic, tar-like or pungent odors.

Chlorination of condensate streams is often used as a means of odor control. This is usually done by mixing bleach plant effluent with the condensate stream. This treatment may in fact give rise to chlorinated compounds by reaction with guaiacol (21). It has recently been reported that tetrachloro-o-benzoquinone and related chloro-catechols, which may be derived from guaiacol, are the principal toxic components in bleached kraft chlorination effluent (22).

Control of the release of these phenolic compounds may be achieved by using high alkalinity in the weak black liquor. All of these phenolics have a pK_a of 10.0-10.5 so that their vapor pressure will be a function of the pH of the system, very similar to the situation reported for methyl mercaptan (23). Higher alkalinity will reduce the amount of phenols in the condensate streams. Conversely, steam stripping of condensates at lower pH values will aid in transferring the phenols to the distillate.

Several terpenes are listed in Table I. These compounds as a class are usually not considered in effluent problems since they are for the most part collected and marketed. However, they do appear in condensate streams, especially the digester relief condensate. This is due mainly to incomplete phase separation in the turpentine decantors which are never 100% effective. In general, the terpenes found in the condensate are similar to those present in the wood before pulping. However, comparisons of turpentine from Douglas fir wood with sulfate turpentine indicates the amount of α- and β-pinene decreases, while limonene as well as several terpene alcohols increase during the pulping process. The changes are summarized in equation 10.



α-pinene β-pinene limonene α-terpineol Fenchyl alcohol borneol

Eq. 10

Other degraded terpenes i.e. methyl furan and 4-(p-tolyl)pentanol-1 are formed by more involved reaction pathways.

SECTION VI

PROCESS DESIGN STUDIES

General Considerations

Prior studies have been reported from these laboratories (24, 25) utilizing steam stripping to reduce terpene and sulfur compound loads in kraft mill condensate streams. These studies showed that by steam stripping, reusable hot water can be obtained, or the odor levels and oxygen demand can be greatly reduced in water to be discharged from kraft recovery systems.

There remain associated with these operations, however, several disadvantages which it would be desirable to minimize. These include (1) the recycling of terpene and sulfur compounds back through the digester to increase concentrations if "sour" condensates are utilized for the steaming of chips as in the Kamyr system; (2) the gradual loss or escape at numerous points in the recovery system, of terpenes and odorous sulfur constituents, as black liquor is concentrated; (3) if air oxidation of weak black liquor is utilized to minimize the above losses, the air effluent from the oxidation system is itself a source of odorous gases.

It is becoming increasingly clear that reduction of water contamination by transferring the burden to air effluent streams is not a satisfactory solution of such problems. Therefore, a modification of the steam stripping process was sought to minimize the problems enumerated above. The concept discussed in the following pages involves the steam stripping of black liquor effluent from a continuous digester while it is still under pressure, in a multi-stage stripping column. The resulting overhead steam from the column, at about 77 psia, has sufficient heating value to be reused as a stripping agent or indirect heat source for steam stripping of various mill condensates. It would

Preceding page blank

contain appreciable quantities of odorous constituents and terpenes, however; and its utilization in this manner requires careful consideration.

Since the completion of these prior steam stripping studies, our knowledge of the volatile consrituents of kraft black liquor has improved considerably, as already reported, and the vapor-liquid equilibrium distribution of some of these has also been clarified (23, 26), allowing for a more complete and more sound evaluation of the overall process. In addition, a study has been completed of the expected release of volatile terpenes, terpineols, and sulfur compounds from kraft recovery systems (27). These results, together with literature sources which have become available since initiating this work, were utilized in the following report of design studies of combined steam stripping of kraft mill recovery system streams. The long term objective of the study is to find the optimum combination of steam stripping column or columns so as to minimize combined capital and operating costs, taking advantage of marketable by-products to decrease the overall costs of controlling effluent water contamination and air pollution.

Steam Stripping of Black Liquor

The steam stripping of black liquor as it leaves the digester would be expected to reduce immediately the concentration of the most volatile constituents, the terpenes, terpineols, methyl sulfide, and, if the pH of the black liquor is 12.0 or below, of methyl mercaptan. These volatiles would, therefore, not be appreciably present through the one or more flash stages, dilute liquor oxidation and multi-effect evaporation. Odors from leakage, etc., during these operations would be decreased, and the resulting condensates would contain fewer volatile constituents, and lower biochemical oxygen demand. In addition, the terpenes should be more amenable to recovery for sale, if this is desired, by isolating the condensate of black liquor stripping from other condensates and controlling the amount of steam used for this

purpose. The study of actual terpene content of various streams of existing kraft mills, Section V of this report, illustrates that in the absence of black liquor stripping, turpentine appears in the second flash stage in continuous digester systems and to some extent, in evaporator condensates as well.

Since methanol was not considered in the prior design studies, an important purpose of the present calculations is to estimate its distribution during black liquor evaporation.

Continuous Kamyr System Stripping Processes

The nature and quantity of terpenes and terpineols present in kraft black liquor is dependent mainly upon the wood species and condition. Methanol, methyl mercaptan and methyl sulfide yield are governed by the methoxyl content of wood lignin and process kinetics. The assumptions and procedures of Tsuchiya and Johanson (27) were adopted for this study. These were modified as necessary to incorporate the possibility for steam stripping of black liquor ("SEKOR stripping column B"), of high-odor condensates ("SEKOR stripping column A"), and of low-odor condensates ("SEKOR stripping column C"). A flow sheet illustrating these possibilities is shown as Figure 3, which incorporates heat recovery and disposal features.

Published material and energy balance information (28) for a continuous Kamyr digester, washers, and flash system producing 550 ADT/D of pulp was combined with additional information on concentrating black liquor by evaporation (29,30) to give a general basis for calculation of the removal of steam volatile substances from black liquor by steam stripping. Pertinent data are shown in Table VII.

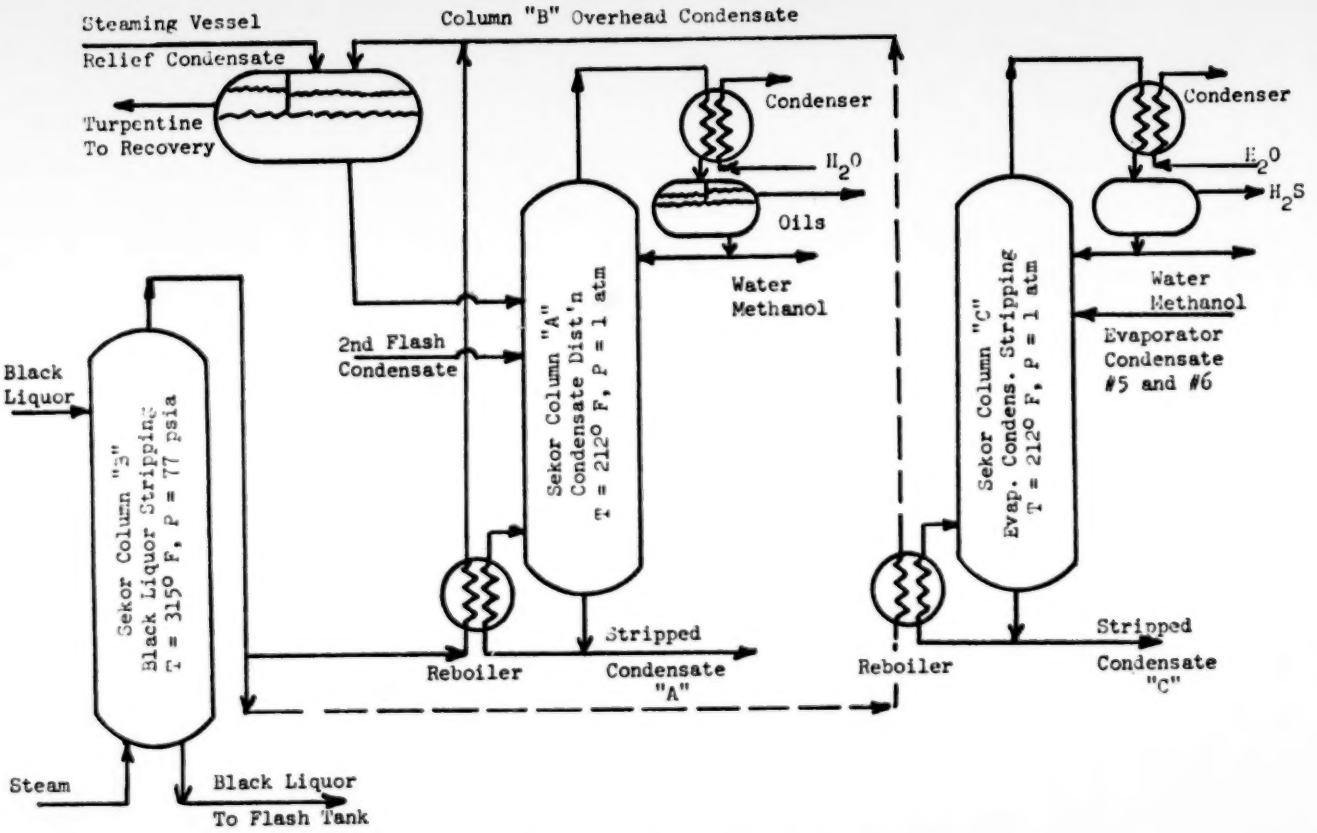


FIGURE 3. Flow System For Combined Steam Stripping Study Utilizing Heat From Black Liquor Stripping.

TABLE VII

Material and Energy Balance for Kamyr Digester, Washers and Flash System

Digester Capacity	550 ADT/D
Black Liquor Flow Rate	481,000 lb/hr
Dissolved Solids	73,200 lb/hr
Per Cent Solids	15.2%
B. L. Temperature	315°F

The major influence of wood species is in the nature and amount of terpenes and in the methanol content. Terpene recovery is estimated arbitrarily for a Western U.S. conifer yielding an assumed average of 1.0 gal terpene per air dried ton of pulp (31).

The methanol yield is based on an average yield of 2.38 gal/ADT or 15.6 lb/ADT as found for Douglas Fir (12), a low methanol-yielding species, and has been superimposed on the original digester effluent stream material balance for this calculation.

Prediction of Stripping Column Performance in Continuous Kraft Mill Recovery Systems

Removal of 90% and 99% of methyl mercaptan from the black liquor digester effluent by steam stripping were chosen for design bases. Methyl mercaptan has an offensive odor which makes its removal from black liquor highly desirable. Upon oxidation, any methyl mercaptan remaining will be converted to dimethyl disulfide which also has an objectionable odor. At a given alkaline pH, the vapor pressure of methyl mercaptan is much higher than that of hydrogen sulfide. However, the hydrosulfide ion concentration in black liquor is so high that larger absolute amounts of hydrogen sulfide will ordinarily be released.

After selection of methyl mercaptan removed as the design basis, the next variable to be considered was the feed to steam ratio, or liquid to gas ratio (L/G). The minimum steam rate corresponds to equilibrium conditions at the rich end of the stripping column (32). Equilibrium data from work done previously at the University of Washington (23, 26) were used for hydrogen sulfide and methyl mercaptan. Two pH levels, 11 and 12, were considered as being representative for black liquor from a continuous digester.

The stripping towers designated as Columns A, B and C in Figure 3, are two-phase continuous contacting devices in which volatile components within the liquid feed are transferred to a counter-current gas phase which, in this case, is steam. For dilute solutions with no chemical reaction occurring, the number of transfer units required for separation is proportional to the logarithmic mean driving force. The black liquor stripping tower "B" has been placed after the digester and before the first flash tank in the process flow sheet. This allows steam stripping under pressure to be utilized, which makes the column overhead stream valuable as a heat medium for columns "A" and "C".

Column height requirements were determined for a range of feed-to-steam ratios of practical interest $20 < (L/G) < 55$. At the lower end of this range, steam costs are high and column height requirements are minimized. At the upper end of the range, steam costs are reduced, but column height requirements increase. Column height is evaluated in terms of the theoretical "number of transfer units" (Ntu) (33). For many common industrial column designs, a transfer unit corresponds to about two actual plates in a plate-type tower, or to about 3 to 6 feet of packing in a packed-type tower.

Results summarized in Table VIII show that the removal of methyl mercaptan is directly dependent upon the pH of the black liquor, and

the column height or the number of transfer units within the stripping column, and the feed to steam or L/G ratio. Dissociation of both methyl mercaptan and hydrogen sulfide increases with increasing pH, rendering them less volatile. For example, for feed steam ratio of 30:1, 90% removal of methyl mercaptan at pH 12 or 99% removal of methyl mercaptan at pH 11 each require 5.3 transfer units. Or for the same feed steam ratio and the same level of methyl mercaptan removal, stripping black liquor at pH 12 requires at least double the number of transfer units required for pH 11. At a constant feed to steam ratio of 30:1 and pH 12, increasing the desired removal of methyl mercaptan from 90% to 99% increases the number of transfer units from 5.3 to 19.1. The capital costs of the column would be almost directly proportional to these numbers. The study, therefore, suggests, based upon the removal of methyl mercaptan, that the pH and feed steam ratio both must be low to minimize capital costs. However, a low feed steam ratio is reflected in an increased steam cost, and a more detailed optimization study would be required to select the actual best conditions.

Utilizing the combinations of per cent removal of methyl mercaptan (90% and 99%), feed to steam ratio (L/G), and column height (Ntu) illustrated in Table VIII, the calculations were extended to include the other major volatile components of interest, hydrogen sulfide, methyl sulfide, methanol, and terpenes. Concentrations of these constituents to be expected in the digester effluent black liquor were known from the prior prediction study (27). Table IX summarizes the results obtained.

TABLE VIII

Tower Height and Process Steam Requirements
for Methyl Mercaptan Removal by
Steam Stripping of Black Liquor

L/G*	Steam Cost** ¢/ton pulp	Transfer Units Required for 90% Removal pH=11	90% Removal pH=12	99% Removal pH=11	99% Removal pH=12
20	50		2.2		5.3
25	39		3.1		9.2
30	33	2.2	5.3	5.3	19.1
35	28	2.9	9.9	7.2	
45	22	5.4		18.5	
55	18	50.			

* Pounds of condensate treated per pound of steam
** Based upon steam cost of $0.50/1000 pounds, cents per ton of pulp produced

Underlined cases are extended in subsequent calculations incorporating further stripping operations, as Cases I, IIa, IIb and III reading left to right.

TABLE IX

Removal of Volatile Constituents by
Steam Stripping of Kraft Black Liquor

	Methyl Mercaptan	Hydrogen Sulfide	Methyl Sulfide	Methanol	Terpenes
Concentration in Digester Effluent, versus pH, lb/ton pulp					
@pH 11	1.40	167	0.228	15.7	13.7/8.0***
12	1.34	166	0.304	15.7	13.7/8.0***
Amount Stripped as percent of Digester Effluent, versus L/G					
@L/G = 20	90 or 99*	-/2.4**	99+	36	99+
25	"	-/1.9	99+	35	99+
30	"	11.3/1.6	99+	25	99+
35	"	9.7/1.4	99+	23	99+
45	"	7.5/-	99+	22	99+
55	"	---	---	--	---

* The bases of calculation, as shown in Table VIII.
** First figure is H_2S stripped @ pH=11; second figure at pH=12.
***Concentration with and without recycling of flash tank vapors to steaming vessel.

Hydrogen sulfide is the most concentrated odorous compound in black liquor and like methyl mercaptan, is also an ionizable substance which shows increasing dissociation with increasing pH. As shown in Table IX, the removal of hydrogen sulfide from black liquor by steam stripping is very dependent upon both pH and feed to steam ratio. For steam rates under consideration in this study, the removal of hydrogen sulfide does not exceed 12% for pH 11 or 2.5% for pH 12. Thus, steam stripping of black liquor will not appreciably decrease H_2S levels in condensate streams from flash tanks and evaporators.

Published vapor equilibrium data for methanol-water (34) indicate that the vaporization equilibrium constant at very low concentrations is about 8, independent of pH and may be assumed independent of ionic strength. The methanol removal, then, depends mainly on the feed to steam ratio. The removal of methanol for flow rates under consideration varies from 22 to 36%. Thus, additional removal of methanol further along the black liquor concentration path may be desirable.

Methyl sulfide and terpenes, which have much higher vaporization equilibrium constants (25) are more than 99% removed in the black liquor stripping column for all cases under consideration.

Four cases from those presented in Tables VIII and IX were chosen for further calculations to extend the predicted distribution of these volatile constituents through the remainder of the black liquor concentration process. These are summarized as Table X.

The distribution of volatile compounds between the vapor and liquid phases of the flash tanks, Figure 4, was calculated as a continuous equilibrium vaporization (35). In the process scheme used here, the overhead product from the first flash tank is fed to the steaming vessel to preheat chips before they enter the digester. The vapor-liquid distribution between condensed steam and steaming vessel relief was also treated as an equilibrium vaporization (36).

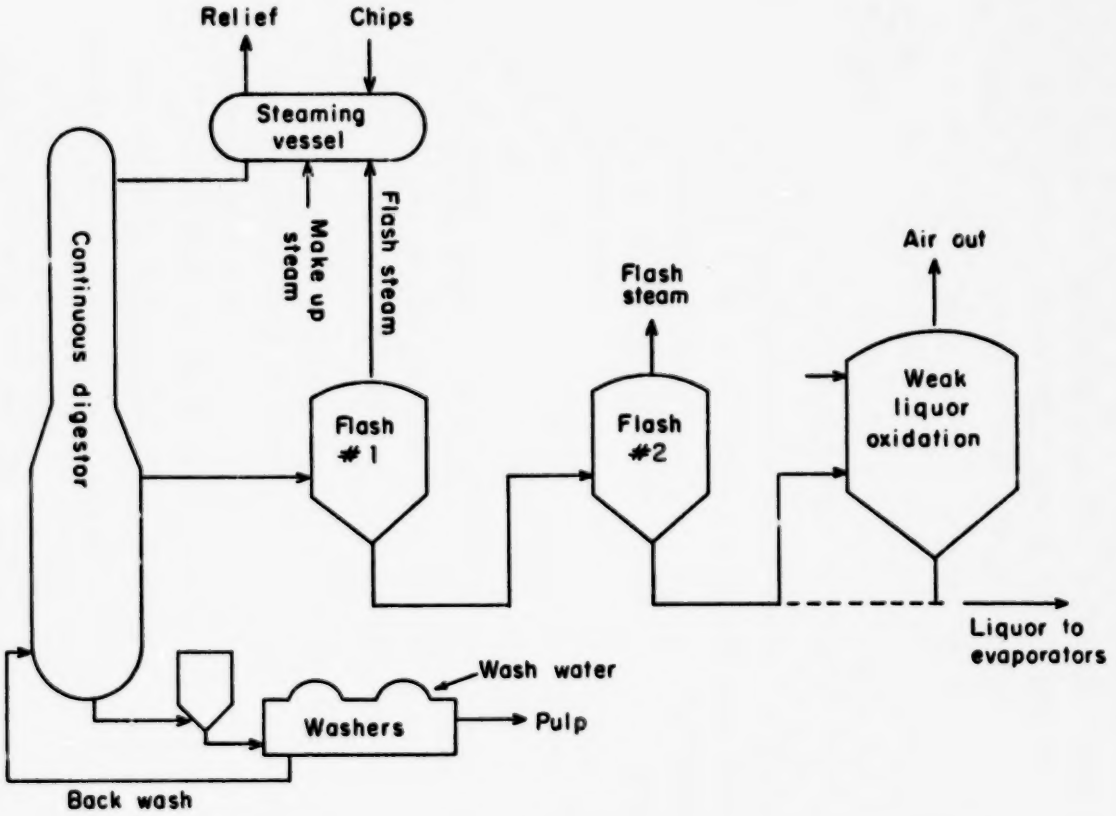


Figure 4. Flash concentration and oxidation steps in black liquor recovery (27).

TABLE X

Operating Parameters of Black Liquor Stripping Column for Cases Extended to Steam Stripping of Condensates

Case	Meth Merc. Removal	Feed: Steam ratio	Ntu	pH	Steam Cost ¢/ADT
I	90%	45	5.4	11	22
IIa	90%	30	5.3	12	33
IIb	99%	30	5.3	11	33
III	99%	25	9.2	12	39

Weak liquor oxidation at 0%, 70% and 95% efficiency was considered for each of the four cases and was subject to the assumptions of reference (27), namely, cocurrent or complete mix flow, and phase equilibrium. For no oxidation, the larger amount of feed to the first two evaporators (#5 and #6, in parallel) was compensated for by arbitrarily increasing the amount of evaporation from these two units.

Calculations of vapor-liquid distribution show that in this flow scheme the only compounds lost in significant quantity with the exit air from the oxidation tower are hydrogen sulfide and methanol. To minimize H_2S emission from this source, high black liquor pH and oxidation efficiency of 95% or above is recommended. The methanol loss is independent of oxidation efficiency and pH and depends only on the flow rate of air through the oxidation system and the entering methanol concentration. If recovery of methanol is to be an economic consideration, the fact that 25% to 30% of the methanol from the digester is lost during oxidation may be very significant.

The oxidized black liquor is subjected to multi-effect evaporation in six stages, followed by direct contact evaporation in the flow system model utilized here, as shown in Figure 5. Calculations were extended through each of the six evaporator stages for each of the four cases,

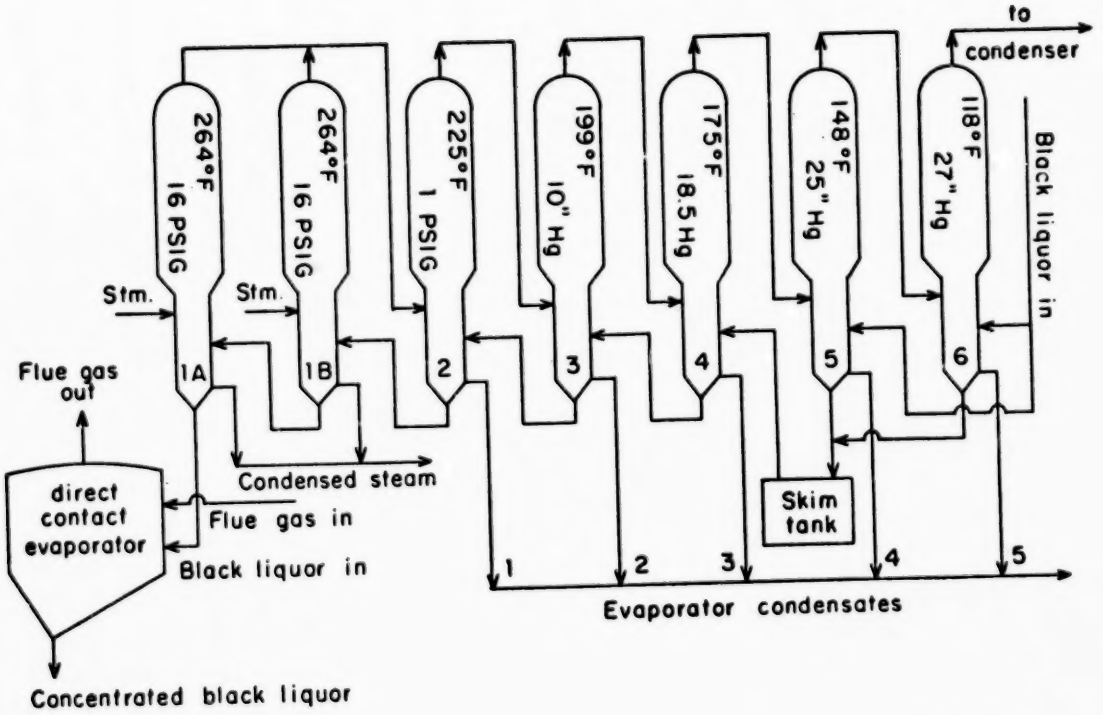


Figure 5. Multieffect evaporation stages and direct contact evaporators (27)

and for each of the three levels of oxidation of 0%, 70% and 95%. These results are summarized and compiled as Tables XI, XII, XIII, and XIV.

Note that the tables show quantitatively much of what has been indicated earlier in a qualitative way. For example, terpenes and methyl sulfide are removed in the black liquor stripping column. Methyl mercaptan is removed to the extent fixed by the design basis for the case under consideration (90% to 99%). Hydrogren sulfide continues to be removed steadily throughout the evaporation process, depending upon the oxidation level and pH. The release of H_2S with the oxidation tower air effluent is decreased about fourfold with pH change from 11 to 12 (131.7 vs 35.4, or 28.2 vs 7.1). A change in oxidation level from 70% to 95% decreases this release approximately fivefold (131.7 vs 28.2, or 35.3 vs 7.1). Methanol volatilizes steadily but at a diminishing extent throughout the multi-effect evaporator train, though after the first two parallel effects (#6 and #5), only about 10% of the original methanol remains and this is almost entirely evaporated in the remaining five stages, to appear in the condensates. A small quantity of dimethyl disulfide is found in the oxidation tower from the remaining methyl mercaptan. This is released with the air from the oxidation system and negligible quantities should appear in subsequent condensates.

Column Requirements for Steam Stripping of Selected Condensates together with Black Liquor Stripping

Energy balances show that the vapors from black liquor stripping are sufficient to strip all condensates depicted in Figure 3 for the 550 ton-per-day pulp mill used as a model. This is shown as being done through indirect heat exchange in a reboiler because of the contaminants in this steam source. The resulting SEKOR B overhead condensate, steaming vessel relief condensate, and No. 2 flash condensate have similar levels of contaminants, and are fed to the stripping column

Table XI

Summary of Volatile Component Distribution

Case I

Source	α-Pinene lb/hr	α Terpineol lb/hr	H_2S [lb.S/hr]			CH_3SH [lb.S/hr]			MeOH [lb/hr]		$(CH_3)_2S$ [lb.S/hr]	$(CH_3)_2S_2$ [lb.S/hr]		
Digester	277	35.8	3589			21.30			357.7		2.7			
*Sekor B overhead	277	35.8	269			19.17			78.7		2.7			
Sekor B bottoms	0	0	3320			2.13			279					
FT-1 overhead (to steam vessel)	0	0	405			1.75			91					
*St.Vess.Relf.	0	0	2915			.38			188					
FT-1 bottoms	0	0	255			.30			46					
*FT-2 overhead	0	0	2660			.08			142					
FT-2 bottoms	0	0	396			1.65			47.9					
Oxidation Level %			0	70	95	0	70	95	0	70 & 95		0	70	95
Ox tower V				131.7	28.2		.022	.0037		107.8			.055	.075
Ox tower L				666.3	104.8		.002	.0003		34.2			.001	.001
Evaps														
*6-overhead			709	179	28	.0392			56.7	12.8				
6-bottoms			621	154	24	.0008			14.3	4.3				
*5-overhead			497	126	19.9	.039			53.7	11.7				
5-bottoms			833	207	32.5	.001			17.3	5.4				
*4-overhead			445	106	16.7				16.7	5.1				
4-bottoms			1009	254	39.9				14.9	4.6				
*3-overhead			379	99.1	15.6				8.9	2.8				
3-bottoms			630	155.3	24.3				6.0	1.8				
*2-overhead			310	80.8	12.7				4.1	1.2				
2-bottoms			320	74.5	11.6				1.9	0.6				
*1B-overhead			159	39.0	6.1				1.3	0.4				
1B-bottoms			160	35.5	5.5				0.6	0.2				
*1A-overhead			43	9.4	1.5				.25	.08				
1A-bottoms			117	26.1	4.0				.35	.12				

All column quantities are in lb/hr (terpenes and methanol) or lb sulfur/hr (sulfur cpds).

Case I - pH=11 (L/G)=45, 90% methyl mercap. removal, Ntu=5.4.

*Streams amenable to steam stripping.

Table XII

Summary of Volatile Component Distribution

Case IIa

Source	α-Pinene lb/hr	α Terpineol lb/hr	H_2S [$\frac{lb.S}{hr}$]			CH_3SH [$\frac{lb.S}{hr}$]			MeOH [lb/hr]		$(CH_3)_2S$ [$\frac{lb.S}{hr}$]	$(CH_3)_2S_2$ [$\frac{lb.S}{hr}$]		
Digester	277	35.8	3582			20.4			357.7		3.6	0		
*Sekor B overhead	277	35.8	57			18.36			89.7		3.6	0		
Sekor B bottoms	0	0	3525			2.04			268		~0	0		
FT-1 overhead (to steam vessel)	0	0	96			1.53			87		~0	0		
*St.Vess.Relf.	0	0	3429			.51			181		~0	0		
FT-1 bottoms	0	0	54			.36			45		~0	0		
*FT-2 overhead	0	0	3375			.15			136		~0	0		
FT-2 bottoms	0	0	94.1			1.44			45.8		~0	0		
Oxidation Level %			0	70	95	0	70	95	0	70 & 95		0	70	95
Ox tower V				35.4	7.1		.039	.0067		103.4			.103	.141
Ox tower L				977.1	161.7		.006	.0008		32.6			.002	.002
Evaps														
*6-overhead			236	69.8	11.6	.065	.001		54.4	12.3				
6-bottoms			1452	418.8	69.3	.010	0		13.6	4.0				
*5-overhead			166	49.3	8.2	.064			51.5	11.3				
5-bottoms			1522	439.3	72.7	.011			16.5	5.0				
*4-overhead			205	56.7	9.3				15.9	4.8				
4-bottoms			2769	801.4	132.7				14.2	4.2				
*3-overhead			269	81.0	13.5				8.5	2.5				
3-bottoms			2500	720.4	119.2				5.7	1.7				
*2-overhead			378	119.6	19.9				3.9	1.2				
2-bottoms			2122	600.8	99.3				1.8	0.5				
*1B-overhead			357	109.1	18.1				1.3	.3				
1B-bottoms			1765	491.7	81.2				0.5	.2				
*1A-overhead			12.4	33.4	5.6				.21	.08				
1B-bottoms			164.1	458.3	75.6				.29	.12				

All column quantities are in lb/hr (terpenes & methanol) or lb sulfur/hr (sulfur compounds).

Case IIa: pH=12, L/G=30, 90% methyl mercaptan removal, Ntu=5.3

*Streams amenable to stream stripping.

Table XIII

Summary of Volatile Component Distribution

Case IIb

Source	α-Pinene lb/hr	α Terpineol lb/hr	H_2S [$\frac{lb.S}{hr}$]			CH_3SH [$\frac{lb.S}{hr}$]			MeOH [lb/hr]		$(CH_3)_2S$ [$\frac{lb.S}{hr}$]	$(CH_3)_2S_2$ [$\frac{lb.S}{hr}$]		
Digester	277	35.8	3589			21.3			357.7		2.7	0		
*Sekor B overhead	277	35.8	406			21.1			78.7		2.7	0		
Sekor B bottoms	0	0	3183			.213			279		~0	0		
FT-1 overhead (to steam vessel)	0	0	388			.175			87		~0	0		
*St.Vess.Relf.	0	0	2795			.038			181		~0	0		
FT-1 bottoms	0	0	245			.030			45		~0	0		
*FT-2 overhead	0	0	2550			.008			136		~0	0		
FT-2 bottoms	0	0	94.1			0.144			40		~0	0		
Oxidation Level %			0	70	95	0	70	95	9	70 & 95		0	70	95
Ox tower V				126.2	27.0		.0022	.0003		103.4			.0055	.0075
Ox tower L				638.8	100.5		.0002	.0003		32.6			.0001	.0001
Evaps														
*6-overhead			679	171.8	27.1	.0039			54.4	12.3				
6-bottoms			596	147.6	23.2	.0001			13.6	4.0				
*5-overhead			476	121.2	19.05	.0039			51.5	11.3				
5-bottoms			799	198.2	31.2	.0001			16.5	5.0				
*4-overhead			427	101.9	16.1				15.9	4.8				
4-bottoms			968	243.9	38.3				14.2	4.2				
*3-overhead			364	95.0	15.0				8.5	2.5				
3-bottoms			604	148.9	23.3				5.7	1.7				
*2-overhead			298	77.5	12.2				3.9	1.2				
2-bottoms			306	71.4	11.1				1.8	0.5				
*1B-overhead			153	27.4	5.8				1.3	0.3				
1B-bottoms			153	44.0	5.3				.5	0.2				
*1A-overhead			42	11.7	1.4				.21	0.08				
1A-bottoms			111	32.3	3.9				.29	0.12				

All column quantities in lb/hr (terpenes, methanol) or lb sulfur/hr (sulfur compounds).

Case IIb - pH=11, L/G=30, 99% methyl mercaptan removed, Ntu=5.3.

*Streams amenable to steam stripping.

Table XIV

Summary of Volatile Component Distribution

Case III

Source	α-Pinene lb/hr	α Terpineol lb/hr	H_2S [$\frac{lb.S}{hr}$]			CH_3SH [$\frac{lb.S}{hr}$]			MeOH [lb/hr]		$(CH_3)_2S$ [$\frac{lb.S}{hr}$]	$(CH_3)_2S_2$ [$\frac{lb.S}{hr}$]		
Digester	277	35.8	3582			20.4			357.7		3.6	0		
*Sekor B overhead	277	35.8	68			20.2					3.6	0		
Sekor B bottoms	~0	~0	3514			.204					~0	0		
FT-1 overhead (to steam vessel)	~0	~0	96			.153			76		~0	0		
*St.Vess.Relf.	~0	~0	3418			.051			157		~0	0		
FT-1 bottoms	~0	~0	54			.036			39		~0	0		
*FT-2 overhead	~0	~0	3364			.015			118		~0	0		
FT-2 bottoms	~0	~0	94.1			0.144			40		~0	0		
Oxidation Level %			0	70	95	0	70	95	0	70 & 95		0	70	95
Ox tower V				35.3	7.1		.0034	.00067		89.9			.0103	.0141
Ox tower L				973.9	161.1		.0006	.00008		28.1			.0002	.0002
Evaps														
*6-overhead			237	69.5	11.5	.0065			47.2	10.7			.0001	.0001
6-bottoms			1445	417.5	69.1	.0010			11.8	3.35			0	0
*5-overhead			165	49.1	8.2	.0064			44.7	9.8				
5-bottoms			1517	437.9	72.4	.0011			14.3	4.25				
*4-overhead			204	56.5	9.2				13.8	4.0				
4-bottoms			2758	798.9	132.3				12.3	3.6				
*3-overhead			268	80.7	13.4				7.4	2.2				
3-bottoms			2490	718.2	118.9				4.9	1.4				
*2-overhead			376	119.2	19.8				3.3	1.0				
2-bottoms			2114	599.0	99.1				1.6	0.4				
*1B-overhead			356	108.7	17.9				1.1	0.3				
1B-bottoms			1758	490.3	81.2				0.5	0.1				
*1A-overhead			11.5	32.0	5.6				.04					
1A-bottoms			164.3	458.3	75.6				.06					

All column quantities expressed as lb/hr (methanol, terpenes) or lb sulfur/hr (sulfur compounds).

Case III: pH=12, (L/G)=25, 99% methyl mercaptan removed, Ntu=9.2

*Streams amenable to steam stripping.

SEKOR A shown. Optional removal of turpentine from Column B condensate and steaming vessel relief condensate is also shown.

The amount and composition of the resultant overhead "concentrate" and of the decontaminated condensate bottoms are shown in Table XV. Quantities of volatile components shown in this table are reported as pounds per air-dried ton of pulp. The table footnote relates this unit of measurement to that of Tables XI to XIV. Column dimensions required for 75% and 90% removal of remaining methanol content are shown in Table XVI. Column conditions are as depicted in Figure 3.

TABLE XV

Case IIa - Composition of Feed and Product Streams of SEKOR A Column

	*Volatile Component in lb/ADT** or lb. sulfur/ADT					
	Water	Terpenes	H_2S	CH_3SH	$(CH_3)_2S$	CH_3OH
Feed Stream						
SEKOR B Overhead	700	13.7	2.5	0.8	0.16	3.9
Steaming Vessel Relief	200	nil	4.2	0.072	nil	2.0
2nd Flash Overhead	780	nil	2.35	0.016	nil	2.0
Overhead Product	5 to 25	13.7	9.0	0.89	0.16	5.9
Stripped Condensate	1655	nil	nil	nil	nil	2.0

* For Fd/stm=5.0, 75% MeOH removal of Table X

** For a 550 ADT per day pulp production lb/hr (.0436) = lb/ADT for any constituent.

Evaporator condensates resulting from concentration of the stripped black liquor also contain some contaminants, chiefly hydrogen sulfide and methanol, the latter chiefly appearing during evaporation from 17% to 22% solids, represented by the No. 5 and No. 6 evaporator condensates. These condensates are shown in Figure 3 as feed to a separate stripping column employing SEKOR B overhead as heat medium. Tables XVII and XVIII summarize resulting overhead and bottoms concentrations, and

required column dimensions for the particular case of 0% oxidation level of case II-a. This column and its required conditions are also shown in Figure 3.

TABLE XVI

Case IIa - SEKOR A Column Design for Condensate Stripping

Fd/Stm	Steam lb/hr	Reflux Ratio	No. Ideal Stages	Column Diameter (ft)	% MeOH Removal
(2.4)min	16,000				75
2.8	13,700	70.4	4.0	5.5	"
5.0	7,700	40.6	4.7	4.5	"
10.0	3,900	19.8 (15.2)min			"
2.5	15,600	70.4	5.0	6.0	90
4.2	9,200	40.6	6.3	4.5	"
8.3	4,600			3.0	"

TABLE XVII

Case IIa - Composition of Feed and Product Streams SEKOR Column C Stripping Evap. Condensates

	*Volatile Component in lb/ADT or lb. sulfur/ADT					
	Water	Terpenes	H_2S	CH_3SH	$(CH_3)_2S$	CH_3OH
Feed Stream #5 and #6 Evap. Cond.	4500	nil	17.5	0.006	nil	4.62
Overhead Product	3 to 15	nil	17.5	0.006	nil	3.47
Stripped Condensate	5055	nil	nil	nil	nil	1.15

* For Fd/Stm = 8.0, 75% MeOH removal.

TABLE XVIII

Case IIa - SEKOR Column C Design for Evaporator Condensate Stripping

Fd/Stm	Steam lb/hr	Reflux Ratio	No. Ideal Stages	Column Diameter (ft)	% MeOH Removal
7.2	14,300	12.8	8.2	5.5	75
8.0	12,800	11.5	11.0	5.0	75

Table XIX compares the total final condensate load, as pounds of volatile contaminants per ADT of pulp, with the corresponding condensate load if no black liquor stripping and no condensate stripping is practiced. The latter information is from the previous study of Tsuchiya and Johanson (27).

TABLE XIX

Comparison of Contaminant Content of Condensates Without and With Steam Stripping

	Total Volatiles Content* lb/ADT Without Stripping	With Stripping
Combined Condensates to 17% B. L. Solids	29.0	2.0
Combined Condensates 17% to 22% B. L. Solids	23.9	1.1

* Includes methanol, terpenes, H_2S, CH_3SH, $(CH_3)_2S$, with sulfur compounds as pounds sulfur equivalent.

Improved Phase Equilibrium and Solubility Data

The prior detailed calculations of volatiles behavior during flash evaporations and steam stripping, and indeed all prior design studies of this system are based upon a simplification of the vapor-liquid equilibrium situation. Simplification is necessary because the actual

number of volatile components is at least fifteen, consisting of several terpenes in addition to α-pinene; several terpineols in addition to α-terpineol; and acetone, ethanol, methyl isobutyl ketone in addition to methanol; together with the four sulfur compounds--hydrogen sulfide, methyl mercaptan, methyl sulfide and dimethyl sulfide. The simplifications were basically to treat the multi-component system as a collection of binary systems with water, utilizing the vapor-liquid binary equilibrium data with water. With all substances except water present only in trace amounts, this simplification may be justifiable. Under conditions of concentration of methanol and terpenes to higher levels, as in the upper sections of stripping column A with reflux, the assumptions involved may not be valid.

An assessment of the validity of these assumptions and an improved method of developing multi-component correlations of equilibrium data to supplant these techniques, has been made by Mr. Robert T. Ruggeri in work supported by this contract and reported in detail as a Master's thesis study (37). Results obtained in this work are discussed in the following pages.

The technique consisted first of reducing the multi-component system to a five-component system, water, methanol, α-pinene, α-terpineol and methyl sulfide, where each compound represents a "family" of compounds similar in polarity and chemical nature. This in turn was shown to be reducable to three ternary systems, because only water and methanol appear in moderate to large concentrations in the industrial problem of interest here. Mr. Ruggeri then developed a technique for predicting the ternary equilibrium behavior for the systems from binary equilibrium data available in the literature or obtained experimentally in the thesis investigation. This technique was based essentially upon the equations of Renon and Prausnitz (38). An added advantage of the approach is that extrapolations of equilibrium relationships from the region of available experimental data (such as 25°C) to the level of

design interest (such as 100°C) is much more sound than the direct extrapolation of curves. Renon's equations are based on the molecular pairwise interactions of closest neighbors. By utilizing such a model, an expression for the activity coefficients of the components was obtained which yielded good results for several molecularly dissimilar systems. For binary systems, Renon's equations for the activity coefficient of the first component are as follows:

$$\ln \gamma_1 = [\delta_{21}(G_{21}/(x_1+x_2G_{21}))^2 + \delta_{12}G_{12}/(x_2 + x_1G_{12})^2] x_2^2, \qquad (11)$$

where

$$G_{12} = \exp(-\alpha_{12}\delta_{12}), \text{ and} \qquad (12)$$

$$G_{21} = \exp(-\alpha_{12}\delta_{21}). \qquad (13)$$

The quantities α_{12}, δ_{12}, δ_{21} may be treated as empirical constants, although α_{12} is related to the coordination number and as such has some physical significance. It is found experimentally, however, that small variations in α_{12} do not significantly effect the ability of Equations (11), (12), and (13) to represent experimental data. Furthermore, the value of α_{12} is characteristic of the types of compounds involved in the 1-2 interaction. This means that the system of Equations (11), (12), and (13) can be considered a two constant equation for the activity coefficient. The Renon equations also enjoy two additional advantages over the Margules type equations: the activity coefficient for the i^{th} component of a multicomponent mixture can be written in terms of binary data only, and the temperature dependence of the empirical constants, δ_{12} and δ_{21}, is found to be linear with reciprocal temperature. Both of these advantages result from the fact that only pairwise nearest neighbor interactions are considered in the Renon liquid model. The disadvantage of the Renon equations is the added computational complexity, but the advantages are enough to justify their use, especially for multicomponent work.

An important advantage the Renon equations hold over the more conventional methods of describing excess molal Gibbs energy (g^E) is that the

Renon constants can be found from linear functions of temperature. From Renon's work the delta constants were defined as follows:

$$\delta_{12} = (g_{12} - g_{22})/RT, \tag{14}$$

$$\delta_{21} = (g_{21} - g_{11})/RT, \tag{15}$$

and

$$g_{12} = g_{21}, \tag{16}$$

where g_{ij} is the energy of interaction between a pair of molecules, i and j. The functions of g, i.e., $(g_{ij} - g_{jj})$, were then determined experimentally to be linear in temperature. Renon demonstrated this temperature dependence for at least two systems over a temperature range of 50°C.

One of the primary advantages of using Renon type equations to describe the nonideality of solutions is that these equations can be generalized to multicomponent systems without making any additional assumptions. The more conventional methods of describing the compositional dependence of activity coefficients is to use power series in mole fraction. Wohl's expansion for g^E, used to describe multicomponent mixtures, involves terms related to molecular interactions. For instance, the constant a_{12} is related to the 1-2 molecular interaction and a_{112} is related to the three-body interaction involving two molecules of component one and one molecule of component two. Wohl's equation for g^E can be considered a power series in volume fraction, and when this equation is fitted to experimental data, as many terms are used as are needed to give the desired accuracy. All the two-body constants of the Wohl equation can be calculated by studying binary solutions, but ternary system behavior may not be represented accurately if only the two-body terms are included in the ternary Wohl expansion. The only way to check the reliability of this equation is to study the ternary system and evaluate the three-body constants. If the two-body constants are large with respect to the three-body constants, the Wohl expansion can be determined from binary data. Both the Van Laar equations and the Margules equations can be derived from Wohl's expansion and,

therefore, their use is governed by similar considerations.

Unlike the Wohl type equations, the Renon expansion of g^E was derived by considering only nearest neighbor two-body interactions. The Renon equation, therefore, can be determined from binary data only, without making any additional assumptions. The multicomponent Renon expression for the excess molal Gibbs energy, for a system of N components is as follows:

$$g^E/RT = \sum_{i=1}^{N} x_i \left(\sum_{j=1}^{N} \delta_{ji} G_{ji} x_j\right) / \left(\sum_{k=1}^{N} G_{ki} x_k\right), \tag{17}$$

where

$$\delta_{ji} = (g_{ji} - g_{ii})/RT, \tag{18}$$

$$g_{ij} = g_{ji}, \tag{19}$$

$$G_{ji} = \exp(-\alpha_{ji}\delta_{ji}), \tag{20}$$

and

$$\alpha_{ji} = \alpha_{ij}. \tag{21}$$

By differentiating Equation (17) appropriately, the following expression is obtained for the activity coefficient:

$$\ln \gamma_i = D_1 + \sum_{j=1}^{N} \left(x_j G_{ij} / \sum_{k=1}^{N} G_{kj} x_k\right) (\delta_{ij} - D_2), \tag{22}$$

where

$$D_1 = \left(\sum_{j=1}^{N} \delta_{ji} G_{ji} x_j\right) / \left(\sum_{k=1}^{N} G_{ki} x_k\right), \tag{23}$$

and

$$D_2 = \left(\sum_{m=1}^{N} x_m \delta_{mj} G_{mj}\right) / \left(\sum_{k=1}^{N} G_{kj} x_k\right). \tag{24}$$

The primary goal of this project was to describe in some way the chemical and phase equilibrium of the mixture of components which might be present in a commercial steam stripper designed for odor reduction of condensates in a kraft pulp mill. Since the number of components in such a piece of equipment is large, a total analysis of the system would require a great deal of time and labor. In order to simplify the

problem, three compounds representing different classes of organic chemicals were chosen: α-terpineol, dimethyl sulfide, and pinene, and each of these three compounds was studied in a ternary system with water and methanol. This fact should not be interpreted to imply that water and methanol do not represent classes of compounds, but rather, that these two chemicals were assumed to be present throughout the column; therefore, they were considered as components of every ternary system. Each ternary system was studied by analyzing only binary systems. Thus, the system of water-methanol-pinene was studied by analyzing the three binary systems of water-methanol, water-pinene, and methanol-pinene. The systems were investigated at two temperatures wherever possible. The glass apparatus used prohibited analysis at pressures above atmospheric; therefore, some systems were analyzed at only one temperature.

Once the binary systems had been analyzed, their behavior was characterized by the use of activity coefficients. The Renon equations were used for this purpose. The Renon method was chosen because it can be generalized from binary data to multicomponent systems without making any additional simplifying assumptions, and because the temperature dependence of the constants can be represented as linear functions of temperature. The basic plan of attack is, then, to study three ternary mixtures which represent mixtures of three classes of organic compounds, and to characterize the behavior of these mixtures with activity coefficients which are functions of composition at constant temperature.

The data collected on all the systems were analyzed basically by computer. Some systems involving only two data points were calculated by hand, but all systems utilizing more than two data points were analyzed with the aid of a computer. Simple programs were written utilizing, wherever possible, Boeing library subroutines available at the University of Washington computer center. All the programs were designed to give some kind of average fit to the data. Usually a

least squares averaging process was used. The solubility data were fit by least squares polynominals in temperature. The Renon equations were fit to the data by the same type of procedure, but the calculations utilized a library program designed to solve a system of non-linear algebraic equations.

The results obtained from the work described previously can be classified into two groups: the binary results calculated from experimental data, and the ternary results predicted from the binary results. The ternary results are of primary concern here, since they are to be essentially derived from the binary results and would be of value in making detailed design calculations for separation columns. Binary system experimental results and computed equation constants based upon the results are shown in Tables XX to XXII.

Figures 6, 7, 8, and 9 show the more important of these ternary equilibrium relationships. Figure 6 shows the only direct ternary equilibrium data available to date superimposed on the ternary diagram results for 25°C. The tie-lines linking liquid phases in equilibrium show reasonable agreement between the experimental and theoretical results. Comparison of Figures 6 and 7 shows the influence of temperature in this methanol-water-α-pinene ternary.

Appraisal of Approaches

Earlier methodology applied to studies of the removal of volatile and odorous components from aqueous streams have been extended to include consideration of more of the volatile components, stripping of black liquor, stripping of condensates in dual columns, and the vapor-liquid equilibrium relationships prevailing in the multi-component system. Some guidelines may be useful as to the extent that one or more of these approaches should be adopted in a given situation.

TABLE XX

Water-Organic Binary System Results

H_2O IN α-TERPINEOL @ 25°C

Average Solubility = 47.65 gm H_2O/l. soln.

H_2O IN α-TERPINEOL @ 58°C

Average Solubility = 27.56 gm H_2O/l. soln.

σ = 1.76 = 6.4%

α-TERPINEOL IN H_2O

Polynominal Order	Constants			
	C_1	C_2	C_3	C_4
1	2.14	6.2×10^{-4}	0.0	0.0
2	3.26	-4.2×10^{-2}	3.6×10^{-4}	0.0
3	4.20	-9.5×10^{-2}	1.3×10^{-3}	-4.8×10^{-6}

Equations:

$$S = C_1 + C_2T + C_3T^2 + C_4T^3$$

T = Temperature °C
S = Solubility (gm α-Terpineol/l.soln.)

PINENE IN H_2O

Polynominal Order	Constants		
	C_1	C_2	C_3
1	1.14×10^{-2}	1.7×10^{-4}	0.0
2	9.95×10^{-3}	2.4×10^{-4}	-7.0×10^{-7}

Equations: Same as for α-Terpineol solubility.

H_2O-DIMETHYL SULFIDE SYSTEM

Liquid Phase	Mole Fraction Water	Temperature
H_2O rich	0.9998	25°C
DMS rich	0.0101	25°C

TABLE XXI

Methanol-Organic Binary System Results

METHANOL-DIMETHYL SULFIDE @ 24°C Mole Fraction Dimethyl Sulfide		METHANOL-DIMETHYL SULFIDE @ 36°C Mole Fraction Dimethyl Sulfide	
Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase
0.046	0.405	0.041	0.435
0.049	0.422	0.041	0.493
0.115	0.581	0.041	0.413
0.115	0.588	0.203	0.664
0.215	0.692	0.203	0.664
0.215	0.685	0.203	0.685
0.297	0.729	0.874	0.874
0.297	0.736		
0.355	0.727		
0.355	0.758		
0.465	0.822		
0.465	0.829		
0.465	0.823		
0.560	0.835		
0.560	0.829		
0.673	0.851		
0.673	0.853		
0.844	0.885		
0.844	0.890		
0.958	0.897		

Methanol-Terpineol System
Activity of Methanol

Liquid Mole Fraction MeOH	Activity of MeOH at 26°C	Activity of MeOH at 44°C
0.773	0.671	0.747
0.788	0.705	-
0.803	0.727	0.771
0.872	0.813	0.843
0.883	0.827	-
0.891	0.840	0.860
0.949	0.915	-
0.953	0.928	0.933
0.958	0.928	0.940
0.974	0.956	-
0.976	0.964	0.962
0.978	0.964	0.966

TABLE XXI (Cont'd)

Methanol-Pinene @ 24°C

Liquid Phase	Mole Fraction Methanol
MeOH rich	0.913
Pinene rich	0.193

TABLE XXII

Summary of Margules Equation Constants For Binary Systems

System	Temperature	Margules Constants B	Margules Constants C
Water (1) - DMS (2)	25°C	6.561	1.951
Pinene (1) - Water (2)	25°C	10.47	-2.648
Methanol (1) - Pinene (2)	25°C	2.870	0.037
Methanol (1) - DMS (2)	24°C	1.442	-0.235
Methanol (1) - α-Terpineol (2)	24°C	-1.363	-0.152

Equations:

$$\ln\gamma_1 = X_2^2 \; B - C(4X_2 - 3)$$

$$\ln\gamma_2 = X_1^2 \; B + C(4X_1 - 3)$$

TABLE XXIII

Summary of Renon Equation Constants For Binary Systems

System	Temperature	Renon Constants α_{12}	Renon Constants δ_{12}	Renon Constants δ_{21}
Water (1) - Methanol (2)	25°C	0.47	-0.162	0.377
Water (1) - Methanol (2)	75°C	0.47	-0.559	0.315
Water (1) - Pinene (2)	25°C	0.007	36.10	-19.85
Water (1) - DMS (2)	25°C	0.005	45.30	-31.36
Water (1) - Terpineol (2)	25°C	0.20	8.903	-0.283
Water (1) - Terpineol (2)	58°C	0.20	8.564	0.275
Methanol (1) - Pinene (2)	25°C	0.034	1.999	1.000
Methanol (1) - Pinene (2)	64°C	0.034	1.037	0.802
Methanol (1) - DMS (2)	24°C	0.74	1.050	2.00
Methanol (1) - Terpineol (2)	26°C	0.27	-1.241	-1.397

Figure 6 Ternary liquid equilibrium results. Concentrations are given in mole fractions. Temperature is 25°C.

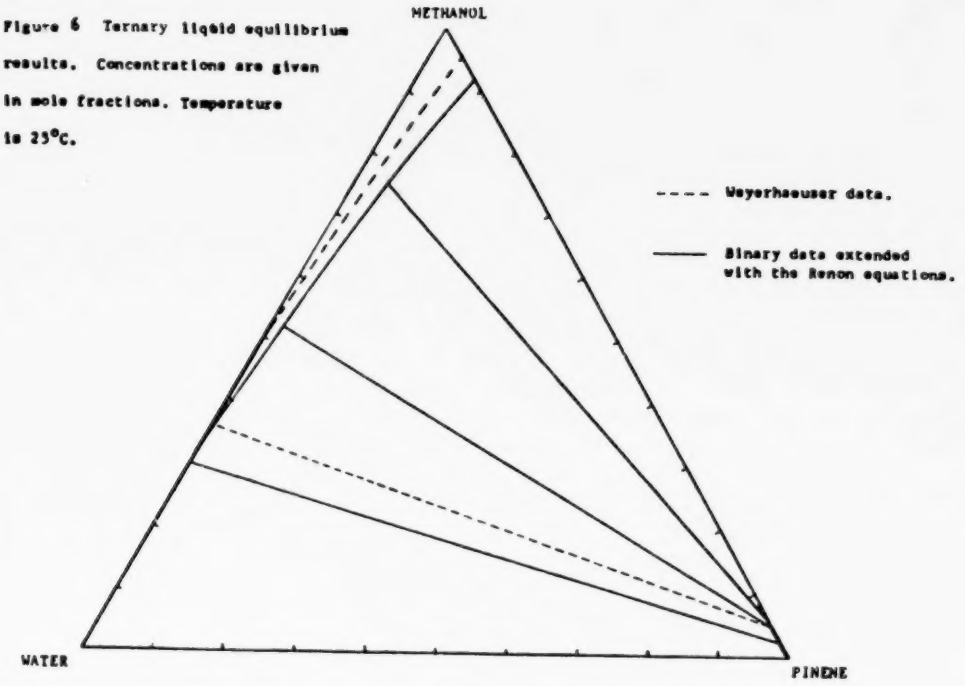
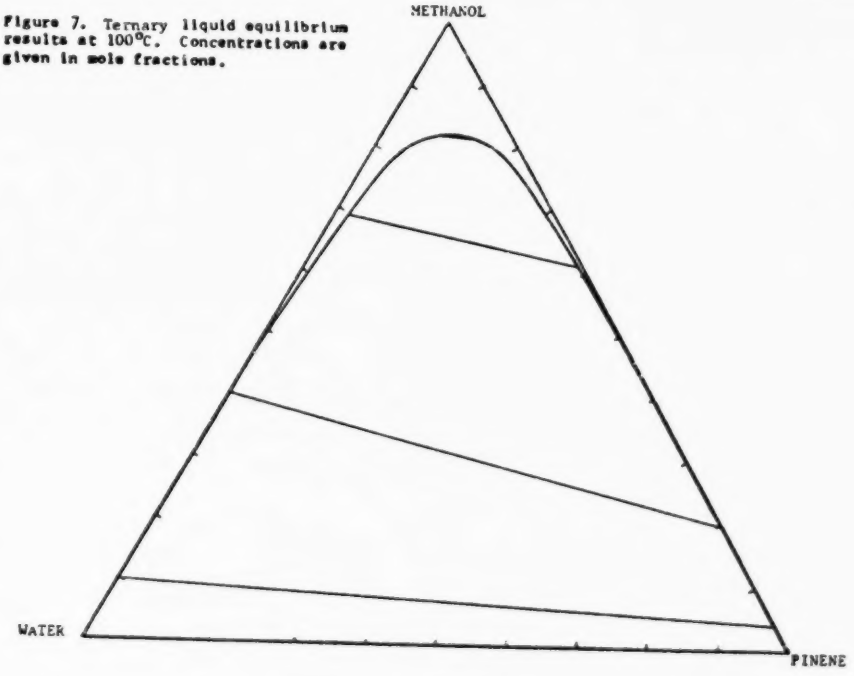


Figure 7. Ternary liquid equilibrium results at 100°C. Concentrations are given in mole fractions.



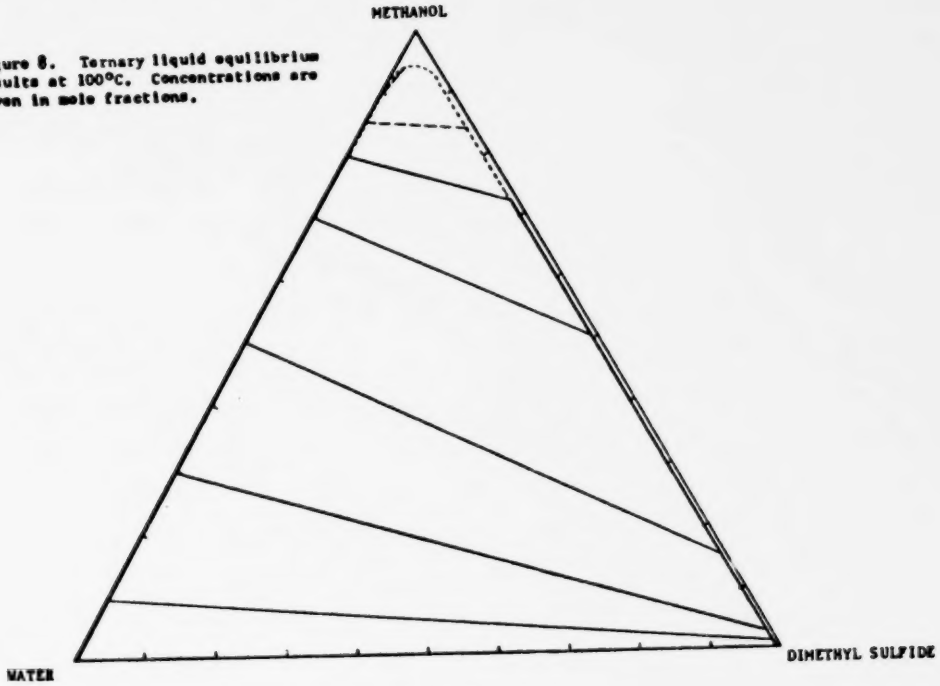


Figure 8. Ternary liquid equilibrium results at 100°C. Concentrations are given in mole fractions.

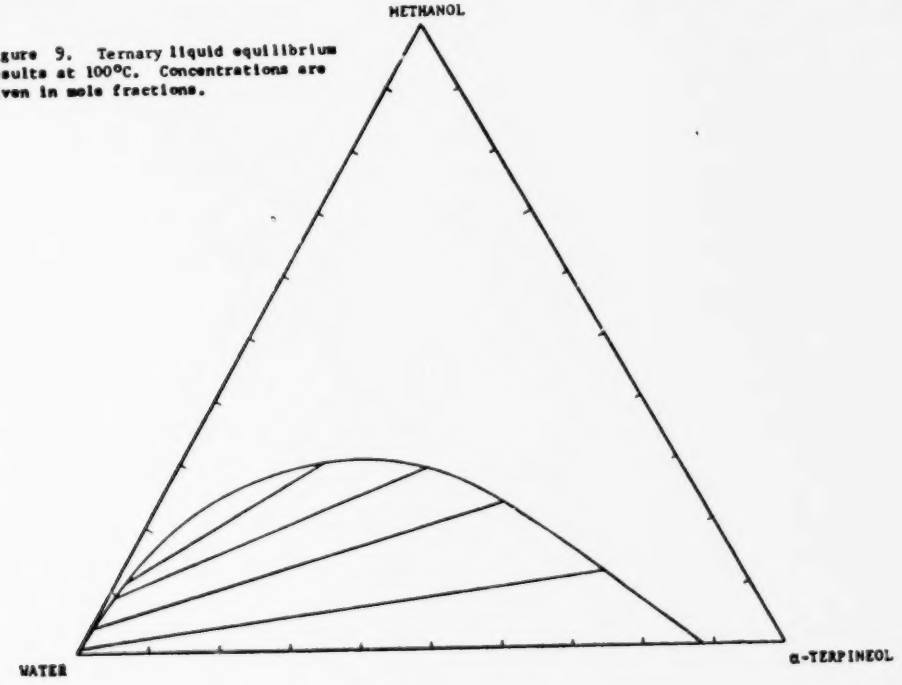


Figure 9. Ternary liquid equilibrium results at 100°C. Concentrations are given in mole fractions.

First, it is the author's belief that in the great majority of applications, steam stripping will be superior to air stripping of condensates. The major advantages are (1) the elimination of the air contamination problem, (2) the possibility of readily and cheaply concentrating the stripped volatile components for burning or other disposal, or for subsequent recovery, and (3) the use of temperature of the condensate in the column as a readily controllable variable, by means of steam pressure. Neither air nor steam stripping are effective for removal of non-volatile compounds.

The use of a single column to strip only those condensates of highest concentration of volatile odorous components, or those to be directly discharged rather than utilized within the mill, remains the most advantageous application of the SEKOR process at minimum cost. The economics of such a system, as described in prior work, Maas, et. al. (25), represents a minimal installation of a column about one-third to one-half the cross-sectional area considered in the present case. If these capital costs are scaled up by a factor of about 3.0 to provide for these differences, the overall costs should remain substantially valid today if costs and turpentine pricing are updated. If methanol is also to be removed to levels less than 2.0 pounds per ton of pulp, then such a column will be inadequate, and two columns are recommended, stripping flash and steaming vessel relief condensates in the first, and about the first two evaporator stage condensates in the second. This would correspond to Figure 3 without the SEKOR B column for stripping black liquor. Costs for such a dual column system would be about double a single column installation, with steam and other utility costs also about double. A bonus in such a column operation is that the evaporation condensates are much more free of hydrogen sulfide and other odorous volatile components than if untreated, and more suitable for reuse or discharge.

The concept of steam stripping black liquor at digester pressure before it is flashed appears to have considerable promise for some situations. Such a system would require pilot scale investigations to corroborate the design studies reported here. It would appear to offer the most promise where recovery of turpentine in high yield is an important considera+ion, and where extreme requirements for extent of removal of methanol and odorous constituents from condensates to be discharged warrants the added cost of black liquor stripping. Costs for such a black liquor stripping column cannot be estimated with confidence without pilot scale study of column operability, but it appears from this design study that such a column would have a cross-sectional area about equal to the combined areas of condensate stripping columns "A" and "C" of Figure 3. Column height would be comparable to these columns. Capital costs would be approximately double that of a two-column condensate stripping system, but steam costs would be only slightly higher, because of the steam re-use feature of the overall system.

SECTION VII

SEPARATION OF SEKOR OILS

General Considerations

In the basic research and development of McCarthy, Hrutfiord, Johanson et al which established the SEKOR process, the observation was made that an oil phase would appear and could be collected separately from the aqueous phase in the overhead stream if the fractionating column overhead water phase was refluxed back to the column. The oil phase was mainly terpene hydrocarbons and organic sulfides, while the aqueous phase was mainly water together with small quantities of water-soluble organics such as methanol, ethanol, and acetone derived from the pulping process. Subsequent research and plans have been based upon this observation. H. Maahs and D. Marsh, working with Professor L.N. Johanson, established in preliminary studies that the terpene hydrocarbons and organic sulfur compounds (methyl sulfide and dimethyldisulfide) could also be removed from condensates by counterflow solvent extraction using petroleum hydrocarbon, as an alternate to steam stripping. The economics in general appeared less attractive than steam stripping, however.

Oil-Water Separations

Early bench scale experiments revealed that SEKOR oils consisted in part of the terpenes ordinarily found in commercial turpentines, with perhaps larger than expected amounts of terpineols. A large fraction, however, (approximately 40%) of oil derived from blow gas condensate consisted of sulfur compounds, chiefly the methyl sulfides. Thus the usual methods of sale or disposal of Kraft turpentines, consisting of less than one per cent sulfur compounds--concentrated acid treatment, chlorination, and caustic washing--seem not to be ideal for the high sulfur concentrations found in SEKOR oils. Furthermore, the high cost and sulfur losses associated with this approach would tend to discourage

Preceding page blank

rather than encourage adoption of the SEKOR process by industry. The terpene hydrocarbons are largely within commercial turpentine boiling range and would have value in commerce as a credit toward the costs of operation of the SEKOR process. The sulfur compounds (chiefly methyl-mercaptan, dimethyl sulfide and dimethyl disulfide) are odorous, unpleasant and noxious. If they can be released from SEKOR terpene oil in concentrated form, they would have value as makeup sulfur in the pulping process, particularly if they could be reduced to hydrosulfide form.

Fractional Distillation would appear to be a logical method of separation of the oils into terpenes and sulfur compounds. However, the several terpenes, terpineols, and sulfur compounds have overlapping volatilities, which makes such separation complex. A partial separation could perhaps be conducted if only α-pinene were to be recovered from all other constituents.

Solvent Extraction of the sulfur compounds from the terpenes, or vice versa, would require a solvent with limited, but different solubility for each class of compound. Over twenty solvent systems were explored as possibilities, with terpene-dimethyl sulfide mixtures ranging from 10-90 to 90-10 molecular ratio. The solvents were found to fall into two groups, the larger group being those having complete miscibility with both terpenes and methyl sulfide, and a smaller group with little or no solubility for either terpenes or methyl sulfides.

Selective Adsorption Separations

This would appear to offer a possible alternative separation method for the two classes of compounds terpenes and organic sulfides. The former compounds are all ring structures, of molecular diameter exceeding 8 angstroms. The sulfur compounds H_2S, CH_3SH, $(CH_3)_2S_2$ are all linear molecules, with diameters approximately 4 to 8 angstroms. Methanol would appear to associate with the sulfur components because of its molecular shape, but its greater polarity makes prediction of its

behavior in this respect difficult. Possible selective agents for this purpose are zeolites or synthetic zeolites, silica gel, and activated carbon. All have at least a substantial portion of their pore diameters within the probably useful 3 to 30 angstrom range.

The zeolites which are crystalline aluminosilicates have long been known in nature, and have long been in use as water softening agents. The synthetic zeolites, however, are a relatively recent development. They differ from the natural crystals in having a controlled structure and a controlled composition. When used as "molecular sieves" (a term coined by J.W. McBain in 1926 for natural zeolites with pores less than five angstroms in diameter), the structure rather than the chemical composition is of most importance. Such zeolites are now available commercially with pore diameters less than 3, 4, 5, 10, or 13 angstroms respectively.

Silica gel and activated carbon have much broader pore size distributions than the synthetic zeolites. Activated carbon or charcoal was not tested in this study.

Solvent Extraction Separation Studies

The exploratory search for suitable solvents, or extractive distillation agents has not been promising. The major difficulty appears to be that the methyl groups of methyl sulfides and mercaptan make their solvent characteristics similar to the terpene hydrocarbons. Consequently a solvent which is miscible with terpenes is also found to be completely miscible with the sulfur compounds. Such solvents tested have included acetone, butyl alcohol, n-butyl ether, chloroform, ethyl alcohol methanol, n-hexane, dimethyl aniline, and pyridine. All of these solvents were found completely miscible with α-terpene - dimethyl sulfide mixtures ranging from 10% - 90% to 90% - 10% in composition. Additional solvents tested with both dimethyl disulfide and dimethyl sulfide, as well as terpene mixture were: carbon disulfide, dimethyl sulfide, benzene, toluene, cyclohexane, carbon tetrachloride, phenol, nitrobenzene and cresol. The same results of complete miscibility were

found. At the other extreme, liquids which are essentially immiscible with terpenes, which include ethylene glycol and water, are also found to dissolve dimethyl sulfide to an extent less than detectable by the techniques used, approximately 0.5%.

A search was conducted for solvents which would selectively remove either the terpenes or the sulfur compounds for use in extraction processes. Both literature search and laboratory experiments with a variety of solvent classes proved negative, in that solubility of the terpenes and of sulfur compounds were too similar in a given solvent to allow for an economically attractive separation process.

Thus extraction systems of promise have not been found. Some possibilities still exist, for example liquid HF and liquid SO_2, as used in the petroleum industry for desulfurizing. These are unattractive as solvents for reasons of refrigeration requirements and toxicity of HF, and are intended for thiophene class sulfur compound removal as well.

Selective Adsorption Separation of Terpenes and Sulfur Compounds

The SEKOR oils consist largely of the two classes of compounds, terpenes and methyl sulfur compounds. The terpenes found in the volatile fractions of Kraft turpentine are substantially all monocyclic (limonene, α-terpineol), or dicyclic (pinenes, carene, camphene). Their molecular diameters thus exceed five angstroms, whereas the molecular diameter of methyl mercaptan is 5.0 angstroms. Methyl sulfides, being linear molecules, should similarly have a molecular diameter normal to the bond directions of about five angstroms. Thus it should be possible to selectively remove the sulfur compounds from the terpenes in a batch or semi-continuous process. One such process, utilized to separate straight chain paraffins from iso-paraffins or naphthenes, is described in reference 39. Experiments were conducted utilizing "Linde" brand molecular sieves (synthetic crystalline alumino-silicates), and silica gel. The molecular sieves have narrow pore size distribution while the silica gel has a broad spectrum of pore sizes. Molecular sieve 3A, 5A, 10A

and 13X were tested. The 3A and 5A materials, with approximately 3 angstrom and 5 angstrom pores, were found non-selective with respect to sulfur compound removal from terpenes. The 10-A and 13X materials, of approximately 8 angstrom and 10 angstrom pores, respectively were found to preferentially retain the sulfur compounds from the terpenes. The extent to which this occurs was determined utilizing packed columns of crushed and pelleted sieve material, and determination of break-through curves using mixtures of α-pinene or commercial turpentine and dimethyl sulfide. Analysis was by means of gas liquid partition chromatography, for which calibration data were established for the above constituents and methanol. Methanol was utilized as a column purge, with regeneration by evaporation of the methanol remaining by heating the column.

Silica gel was also found to retain selectively the sulfur compounds, with techniques much as utilized with the molecular sieves.

Laboratory experiments were planned such as to furnish suitable design data for larger scale application. Continuous adsorption techniques have been developed and reported in the literature utilizing moving bed or sequencing feed and withdrawal lines. It is likely, however, that for the scale of operation required for processing SEKOR oils a batch sequence technique would prove preferable. In either case, required design data would include break-through curves for both adsorption and regeneration steps, at a given temperature, flow rate, and column length. The S shaped break-through curve for adsorption represents the transition from purified terpene effluent and effluent having the composition of the feed material, as a result of exhaustion of the column capacity. Similarly, the break-through curve for regeneration represents the transition between methanol-sulfur compound mixtures and pure methanol, signifying regeneration is complete.

Break-through curves have been obtained for silica gel and for 10 angstrom molecular sieve, with α-pinene methyl sulfide mixtures. For

the latter adsorbent, successful regeneration by elution with methanol, followed by drying has also been demonstrated. This regenerated molecular sieve is found to be essentially the same as the original material, giving almost superposition of adsorption break-through curves.

The most effective adsorbent found for selectively removing, for example, dimethyl disulfide from α-pinene was silica gel, with 13 to 20 ml. of solute-free terpene (α-pinene) recovered from a 29 ml. (0.64 cm by 90 cm) gel-packed column before the appearance of the break-through curve for dimethyl disulfide. Much less effective separation was obtained using eight Angstrom and ten Angstrom molecular sieves. The five Angstrom sieve material was found to have no selectivity for sulfur compound removal.

The finding that silica gel was superior as a selective adsorbent for methyl sulfides compared to molecular sieves was unexpected. It was earlier postulated that the narrow size ranges of pores in the sieves should be ideal for removing the straight chain methyl sulfides from the ring-structure terpenes. Silica gel has a broad range of pore sizes, and its superior effectiveness suggests factors other than molecular shape are more important in this separation.

Twenty-five sets of break-through data were obtained all at room temperature, comprising four adsorbents, three flow rates and four sulfur compound-terpene concentrations. The more significant data obtained are summarized in Table XXIV. Additional data, together with a discussion of equivalent mass transfer coefficients, and application to possible scale-up of results, are available in the Master's Thesis of Kap Kyun Kim (40). It is apparent from Table XXIV that silica gel is superior as a selective adsorbent to any of the molecular sieves tested.

This is shown by the larger volume of terpenes which can be passed through the column before the appearance of the sulfur compound (at 5%

of its influent concentration). An additional indication of superiority is the shorter break-through zone height for silica gel.

TABLE XXIV

Summary of Break-Through Data for
Selective Adsorption of Dimethyl Disulfide from Terpenes

*Adsorbent	Pore Radius Å	Mole. % $(CH_3)_2S_2$ in Terpene	Flow Rate ml. to Breakthrough Zone g./cm^2 hr	5%	95%	Ht., cm
Molecular Sieve 5A	5	20	85	0	1	---
Molecular Sieve 10A	8	5	35	2.5	5	50
"	8	20	35	1.0	3	80
"	8	20	85	0.7	5	110
Molecular Sieve 13X	10	20	35	0.3	3	105
	10	20	85	0.3	4	130
Silica Gel	15-100	20	35	20.0	25	18
"	15-100	20	85	17.0	24	30
"	15-100	20	170	15.0	24	45
"	15-100	30	85	13.2	16	15
"	15-100	30	170	13.1	16.5	17

* Adsorption column: glass, 0.64 cm x 90 cm, filled with crushed (24-200 mesh) molecular sieve (20 grams) or with 28-200 mesh silica gel (22 grams). All experiments conducted at room temperature (72°F).

Appraisal of Approaches

For only moderate contamination of the turpentine fraction by sulfur compounds and methanol, the "brute force" method of chemical destruction by oxidation of the impurities followed by water washing would appear to be still preferable to the methods explored here. For higher concentrations of contaminants, selective adsorption would appear to offer more promise than solvent extraction and also more than fractional distillation unless α-pinene is the only major constituent to be recovered by distillation.

For selective adsorption the higher cost of molecular sieves, together with the frequency of regeneration required (because of early break-through of solute) suggests that economic feasibility for this adsorbent is unlikely in this application. There may be some possibility of a feasible process based upon silica gel, however. For example, utilizing the data for silica gel adsorbent, and a 20% methyl sulfide 80% terpene feed mixture flowing at 170 grams per hour per cm^2 of column cross section, 15 ml. of effluent is collected before break-through occurs. This is equivalent to the purification of about 1000 gallons of SEKOR oil charged over a period of six hours to a gel-packed column of 2-ft diam. x 10 ft height, before regeneration is required. This would represent the oil production of a large Kraft mill.

Regeneration of the adsorbent was conducted in the laboratory study utilizing methanol to elute the dimethyl disulfide (as well as the retained terpenes). This polar material was found to be highly effective in displacing the dimethyl disulfide, with the concentration of the latter in the silica gel column effluent falling from 65 mole per cent to less than 1 mole per cent. Although methanol is not the only possible eluent (heating, steam, air or water may be used) it is of interest because it does not introduce a new air contamination problem, is a possible by-product of the SEKOR process, and can be separated from the eluted methyl sulfides by distillation. Alternatively, a continuous industrial process (moving bed or multi-feed column) may be visualized, though it is probable that for the application to steam stripping the batch cyclic process would be simpler and more promising.

SECTION VIII

ACKNOWLEDGEMENTS

The financial support of this investigation by the Environmental Protection Agency Office of Research Monitoring is gratefully acknowledged.

During the course of this study useful discussions were held with a number of people, these included Professor K.V. Sarkanen, Dr. Josef Gratzl, Dr. Wolfgang Glasser and Dr. Kaj Forss of the University of Washington as well as John Van Vessen and James Leonard of the Weyerhaeuser Company. Collaborators on the project who have given invaluable assistance to the investigation were Ms. Juanita Collins, H.R. Monahan, J.T. Ruggeri, Kap Kim and Donald Wilson.

Assistance of the member mills of the Northwest Pulp and Paper Association is also acknowledged.

SECTION IX

REFERENCES

1. Hrutfiord, B.F. and McCarthy, J.L., "SEKOR I: Volatile Organic Compounds in Kraft Pulp Mill Effluent Streams." Tappi 50, No. 2, 82-85 (1967).

2. Bethge, O., and Ehrenborg, L., "Identification of Volatile Compounds in Kraft Mill Emissions." Svensk Papperstid., 22, 347-350 (1967).

3. Wilson, D.F. and Hrutfiord, B.F., "SEKOR IV. Formation of Volatile Organic Compounds in the Kraft Pulping Process." Tappi 54, No. 7, 1094-1098, (1971).

4. Marvell, E.E. and Wiman, R.E., "4-(p-Tolyl)-1-pentanol in Douglas Fir Pulping Products." J. Org. Chem., 28, 1542-1545 (1963).

5. Leonard, J., Weyerhaeuser Company, personal communication.

6. Cabauatan, E.Q., "Monoterpenes in Douglas Fir Needle Oil, Wood Turpentine and Crude Sulfate Turpentine." M.S. Thesis, University of Washington (1969).

7. Sarkanen, K.V., Hrutfiord, B.F., Johanson, L.N., and Gardner, H.S., Kraft Odor," Tappi, 53, No. 5, 766-783 (1970).

8. Ruus, L., "Study on Pulp Mill Effluent." Svensk Papperstid., 19 751-755 (1964).

9. Turner, B.G. and van Horn, J.T., Southeastern Section TAPPI Meeting, March, 1969.

10. Seppovaara, O. and Hynninan, D., "On the Toxicity of Sulfate-Mill Condensates." Paperi ja Puu, 1, 11-23 (1970).

11. McDermott, G.N., Tech. Bull. No. 72, NCASI, November 1954, revised, 1970.

12. Wilson, D.F., Johanson, L.N., and Hrutfiord, B.F., "Methanol, Ethanol and Acetone in Kraft Pulp Mill Condensate Streams," Tappi, 55, No. 3, 1244-1246 (1972).

13. Cade, S.C., Hrutfiord, B.F., and Gara, R.I., "Identification of the Primary Attractant for Gnathotrichus Sulcatus Isolated from Western Hemlock Logs." J. Econ. Entom., 63, 1014-15 (1970).

14. Clayton, D., "The Alkaline Degradation of Some Hardwood 4-o-Methyl-D-Glucuronoxylans." Svensk Papperstid., 4, 115-124 (1963).

Preceding page blank

15. Hrutfiord, B.F. and Wilson, D.F., "Turpentine Concentrations in Kraft Mill Condensate Streams." MMS in EPA review, August (1972).

16. Dres, J., Russell, J., and Bajak, H.W., Sulfate Turpentine Recovery. Pulp Chemicals Association, New York (1971).

17. Liu, L.Y., "Turpentine Collected from Continuous Digester." Pulp and Paper Int., 12, No. 3, 55-57 (1970)

18. Graham, K., "Anaerobic Induction of Primary Chemical Attractancy for Ambrosia Beetles." Can. J. Zool., 46, 905-908 (1968).

19. Wasserman, A.E., "Organoleptic Evaluation of Three Phenols Present in Wood Smoke." J. Food Sci., 31, 1005-1010 (1966).

20. Leonardos, G., Kendall, D., and Barnard, N., "Odor Threshold Determinations of 53 Odorant Chemicals." J. Air Poll. Control Assoc., 19, 91-95 (1969).

21. Sarkanen, K.V., "The Chemistry of Delignification in Pulp Bleaching." Pure and Applied Chemistry, 5, 221-233 (1962).

22. Das, B.S., Reid, S.G., Betts, J.L., and Patrick, K., J. Fisheries Res. Board Can., 26, 3055-2067 (1969).

23. Shih, T.T.C., Hrutfiord, B.F., Sarkanen, K.V. and Johanson, L.N., "Methyl Mercaptan Vapor-Liquid Equilibrium in Aqueous Systems as a Function of Temperature and pH." Tappi, 50, No. 12, 634-638 (1967).

24. Matteson, M.J., Johanson, L.N., and McCarthy, J.L., "Steam Stripping of Volatile Organic Substances from Kraft Pulp Mill Effluent Streams." Tappi, 50, No. 2, 86-91 (1967).

25. Maahs, H.G., Johanson, L.N., and McCarthy, J.L., "SEKOR III. Preliminary Engineering Design and Cost Estimates for Steam Stripping Kraft Pulp Mill Effluents." Tappi, 50, No. 6, 270-275 (1967).

26. Shih, T.T.C., Hrutfiord, B.F., Sarkanen, K.V., and Johanson, L.N., "Hydrogen Sulfide Vapor-Liquid Equilibrium in Aqueous Systems as a Function of Temperature and pH." Tappi, 50, No. 12, 630-634 (1967).

27. Tsuchiya, G.S. and Johanson, L.N., "Prediction of Generation and Release of Odorous Gases from Kraft Pulp Mills." Tappi, 55, No. 5, 777-783 (1972).

28. Hubbe, P.D., "Digester Problem Statement," Tappi, 49, No. 5, 61A-69A (1966).

29. Wetherhorn, D., "The Calculation of Evaporator Heat Balances from Operating Data." Tappi, 47, No. 2, 168A-171A (1964).

30. Libby, C. Earl (Ed.), Pulp and Paper Science and Technology, Vol. I. McGraw Hill, New York, (1962).

31. Drew, J. and Plyant, G.D., Jr., "Turpentine from the Pulpwoods of the United States and Canada." Tappi, 49, No. 10, 430-438 (1966).

32. Bennett, C.O. and Meyers, J.E., "Momentum, Heat and Mass Transfer." McGraw-Hill, New York (1962) p. 531.

33. Treybal, R.E., "Mass Transfer Operations, 2nd Ed.," McGraw-Hill New York (1968) p. 252.

34. Chu, J.C., "Distillation Equilibrium Data." Reinhold Publishing Corp., New York, New York (1950).

35. Perry, J. "Chemical Engineers Handbook, 4th Ed." McGraw-Hill, New York (1963) p. 13-20.

36. Tsuchiya, G., "The Generation and Loss of Volatile Constituents in the Kraft Pulping Process." M.S. Thesis, University of Washington (1970).

37. Ruggeri, R.T., "Phase Equilibrium of Kraft Mill Effluent Streams." M.S. Thesis, University of Washington (1971).

38. Renon, H. and Prausnitz, J.M., "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures." AIChE Journal, 14, 135-144 (1968).

39. Broughton, D.B., "Molex: Case History of a Process." Chem. Eng. Prog., 64, No. 8, 60-65 (1968).

40. Kim, K.K., "Separation of Methyl Sulfides from Terpenes of Kraft Pulp Mill Condensate Streams by Adsorption." M.S. Thesis, University of Washington (1969).

SECTION X

PUBLICATIONS AND PATENTS

The following publications have been produced or are anticipated to be produced as a result of this project:

SEKOR IV. Formation of Volatile Organic Compounds in Kraft Pulping Process. Wilson, D.F. and Hrutfiord, B.F., Tappi, 54, No. 7, 1094-1098, (1971).

SEKOR V. Methanol, Ethanol and Acetone in Kraft Pulp Mill Condensate Streams. Wilson, D.F., Hrutfiord, B.F., Johanson, L.N., Tappi, 55, No. 8, 1244-1246 (1972)

SEKOR VI. Turpentine Concentrations in Kraft Mill Condensate Streams. Hrutfiord, B.F., and Wilson, D.F. Accepted for publication in Pulp and Paper Magazine of Canada (1973).

Thesis Wilson, D.F., "Volatile Organic Compounds in Kraft Pulping." M.S. Thesis, University of Washington, (1970).

Thesis Ruggeri, R.T., "Phase Equilibrium of Kraft Mill Effluent Streams." M.S. Thesis, University of Washington (1971).

Thesis Kim, K.K., "Separation of Methyl Sulfides from Terpenes of Kraft Pulp Mill Condensate Streams by Adsorption." M.S. Thesis, University of Washington, (1969).

It appears that no patentable developments have arisen from the present study.

Preceding page blank

SECTION XI

GLOSSARY

1. Black Liquor -- Spent pulping chemicals and dissolved wood components resulting from kraft pulping.
2. Blow Gas Condensate -- Condensed steam resulting from discharging digester contents at high temperature.
3. Condensate -- General term for liquid resulting from condensing steam etc. to water and organic liquids.
4. Crude Sulfate Turpentine -- Mixture of terpenes and sulfur compounds isolated from kraft digester.
5. Digester Relief Condensate -- Condensate from condensing vented steam and relief gas from kraft digesters.
6. Evaporators -- Units which concentrate black liquor, giving evaporator condensate as one product.
7. Kraft Pulping -- Delignification of wood with sodium hydroxide and sodium sulfide.
8. Liquid to Gas Ratio -- (L/G) The ratio on a weight basis of the liquid being stripped in a column to the gas (steam) used for stripping.
9. SEKOR -- Stripping Effluent for Kraft Odor Reduction.
10. Steam Stripping -- Removal of volatile components by vaporizing with steam.
11. Transfer Unit (Ntu) -- A vertical height of packed column which accomplishes stripping equivalent to that of a theoretically perfect contacting stage.
12. Vapor-Liquid Equilibrium Constant -- A numerical constant defining the ratio of concentration in vapor in equilibrium with the concentration in liquid phase.

Preceding page blank

☆ U. S. GOVERNMENT PRINTING OFFICE: 1973—514-155/300